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(54) SPHERICAL CORUNDUM PARTICLES, PROCESS FOR THEIR PRODUCTION, AND HIGHLY HEAT-CONDUCTIVE RUBBER OR PLASTIC COMPOSITION CONTAINING THEM.

(57) Spherical corundum particles comprising single particles of 5 to 35  $\mu\text{m}$  in average particle size having no cutting edges. They can be produced by mixing pulverized alumina of a specific particle size with at least one of a halogen compound, a boron compound, and alumina hydrate, heat-treating the mixture at 1,000°C or above, and crushing the product. A highly heat-conductive rubber or plastic composition is obtained by compounding the particles, which is useful as semiconductor sealing materials, etc.

Fig. 1A



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SPECIFICATION

SPHERICAL CORUNDUM PARTICLES, PROCESS FOR  
PREPARATION THEREOF AND RUBBER OR PLASTIC  
COMPOSITION HAVING HIGH THERMAL CONDUCTIVITY  
AND HAVING SPHERICAL CORUNDUM PARTICLES  
INCORPORATED THEREIN

TECHNICAL FIELD

The present invention relates to spherical corundum particles without cutting edges, and having an excellent less abrasive property and flow characteristic and 5 valuable as a filler for a sealing material for electronic parts, a finishing additive or base material, a starting material of a wrapping material, and an additive or base material for refractories, glass or ceramics, a process for the preparation of such corundum particles, 10 a rubber or plastic composition having a high concentration of such corundum particles incorporated therein, and having a high thermal conductivity and a low thermal expansion coefficient, and an electrical or electronic part formed by using this rubber or plastic composition. 15

BACKGROUND ART

Recent increases in the degree of integration and density in electronic parts have increased the power consumption per chip, and therefore, an important problem has arisen of how efficiently the generated heat 20 is radiated or how effectively the elevation of the temperature is suppressed. Accordingly, the development of a material having an excellent thermal conductivity, which is suitable as an insulating sealing material for semiconductors, a material for a substrate on which 25 parts are mounted, and a peripheral material such as a heat-radiating spacer, is demanded.

Another problem concerning heat is how to best maintain the conformity of the thermal expansion coefficient of an element and of an insulating material for

sealing the element. If there is a difference in the thermal expansion coefficient, the thermal stress is repeatedly applied to the bonding portion by the heat cycle when the operation of an integrated circuit (IC) 5 is stopped with the result that the element is damaged. In general, since a resin has a high thermal expansion coefficient, an inorganic filler having a low thermal expansion coefficient is incorporated into the resin to match the thermal expansion coefficient with that of the 10 element.

For example, an epoxy resin containing about 70% by weight of fused silica is generally used as an insulating sealing material for a large-scale integrated circuit (LSI), because of a low thermal expansion coefficient 15 and a good conformability. However, since fused silica has an extremely low thermal conductivity, this epoxy resin material is not suitable for use in a field where heat radiation is very important. Accordingly, a composition having a thermal conductivity of about  $60 \times 10^{-4}$  cal/cm.sec. $^{\circ}$ C, which is formed by filling a large 20 amount of crystalline silica having a high thermal conductivity, is already in practical use. However, crystalline silica having a high thermal conductivity has a defect of a high thermal expansion coefficient. 25 Therefore, the above two problems concerning heat, that is, the problems of heat radiation and thermal expansion conformation, cannot be solved by the use of fused silica or crystalline silica alone.

When fused silica and crystalline silica are 30 simultaneously incorporated, since crystalline silica has a high Mohs hardness and comprises pulverized particles having irregular sharp cutting edges, if the amount of crystalline silica incorporated is increased, the flowability of the composition is drastically 35 reduced and the wear of a kneader or a forming mold is greatly increased, and therefore, the amount of crystalline silica incorporated is restricted. As a means of

reducing the wear, a method can be mentioned in which fused silica having a specific particle size distribution and a low abrasive property is used as a coarse particle fraction and mixed with a fine particle fraction of 5 crystalline silica having a specific particle size distribution, to provide a composition having an excellent flowability and a reduced wear of a mold, as disclosed in Japanese Unexamined Patent Publication No. 58-164250. However, even in this composition, a 10 reduction of the thermal conductivity due to fused silica cannot be avoided.

At present, even in a sealing material having a high thermal conductivity, the thermal conductivity is  $60 \times 10^{-4}$  cal/cm·sec·°C at highest, and a level of  $100 \times 15 10^{-4}$  cal/cm·sec·°C desired as the next target cannot be reached by using crystalline silica. Accordingly,  $\alpha$ -alumina, aluminum nitride, and silicon carbide are under consideration as the filler having a higher thermal conductivity than that of crystalline silica, 20 and alumina is promising as the substitute for silica because alumina is relatively inexpensive, has a stable quality, and has a good general-purpose property.

However, in view of the characteristics of existing alumina, existing alumina cannot be considered suitable 25 as a filler for rubbers or plastics. For example, alumina prepared according to the Bayer process consists of irregular-shaped or plate-like primary particles having a size of several  $\mu\text{m}$  to about 10  $\mu\text{m}$  at largest. Since this alumina has a large oil absorption, the 30 filling property in rubbers or plastics is poor and the amount filled is limited to about 80% by weight, such that if alumina is incorporated, for example, into an epoxy resin, the thermal conductivity is  $60 \times 10^{-4}$  cal/cm·sec·°C at highest. It is known that alumina 35 formed by pulverizing electrofused alumina or sintered alumina is usable as a material of an abrasive or refractory. Since alumina of this type consists of

dense corundum particles and the particle size can be optionally adjusted within a broad range of from a fine particle size to a coarse particle size of scores of  $\mu\text{m}$ , the oil absorption is small and the filling property in 5 rubbers or plastics is excellent. However, the pulverized particles of alumina of this type have many sharp angles and corundum ( $\alpha\text{-Al}_2\text{O}_3$ ) has a high Mohs hardness. Therefore, the abrasive property is larger than that of crystalline silica having the same particle size, and 10 corundum has a defect in that bonding wires or semi-conductor elements are damaged thereby.

A rounded spherical shape having no cutting edges is desirable for alumina particles. As the process for preparing spherical alumina particles, a flame-spraying 15 process is known in which alumina according to the Bayer process is sprayed into a high-temperature plasma or oxyhydrogen flame, and the alumina is fused and then rapidly cooled to form spherical particles. However, this process is economically disadvantageous in that the 20 heat consumption is large, and although the obtained alumina is composed mainly of  $\alpha\text{-Al}_2\text{O}_3$ , it generally contains  $\delta\text{-Al}_2\text{O}_3$  as a subsidiary component. The presence of this subsidiary component is unpreferable because the 25 thermal conductivity of alumina is decreased by the subsidiary component.

As a means for solving the foregoing problems of the conventional techniques, several processes have been proposed for preparing  $\alpha\text{-Al}_2\text{O}_3$  (corundum) particles having a particle size larger than 5  $\mu\text{m}$  and a regular 30 shape. For example, Japanese Examined Patent Publication No. 60-33763 discloses a process in which aluminum hydroxide having a high sodium content is preliminarily dehydrated, a specific mineralizing agent is added to the dehydration product, and the mixture is calcined in 35 a rotary kiln to obtain coarse particles of alumina. Furthermore, Japanese Unexamined Patent Publication No. 58-181725 discloses a process in which a mineralizing

agent containing fluorine and/or boron is added to dry-type absorption alumina and the mixture is calcined in a rotary kiln to obtain similar coarse particles of alumina. However, coarse particles of alumina prepared 5 according to these processes have a shape including regular cutting edges, as shown in the drawing (microscope photograph) of Japanese Unexamined Patent Publication No. 58-181725, and do not possess a rounded spherical shape. Moreover, Japanese Unexamined Patent 10 Publication No. 56-35494 (U.S. Patent No. 4,307,147) discloses a substrate having a covering film composed of a dispersion of polygonal corundum particles in an organic polymer. These corundum particles, however, are angular and do not possess a rounded spherical shape.

15 It is considered that, if spherical corundum particles in which sharp cutting edges are eliminated to reduce the abrasive and wearing properties are used and incorporated as a filler in a resin, a rubber or plastic composition having a good filling property, a reduced 20 abrasive and wearing property, an excellent thermal conductivity, and a high thermal conductivity optimal for an insulating sealing material or the like, will be obtained. However, the kind of the resin in which such spherical corundum particles are to be incorporated, the 25 amount added of the particles, and the incorporation method have not been investigated in detail, and a rubber or plastic composition having a high thermal conductivity and practically usable as a sealing material has not yet been developed.

30 DISCLOSURE OF THE INVENTION

Under this background, research was made into the developing of corundum composed of particles having reduced abrasive and wear properties, which is suitable as a filler, a scratch-free wrapping material or a base 35 material of a ceramic or refractory material, without degradation of the inherent characteristics of corundum particles, such as thermal conductivity, electrical

insulating characteristic, and hardness, and as a result, the present invention was completed.

More specifically, in accordance with the present invention, there are provided (1) spherical corundum

5 particles consisting substantially of single particles having an average particle size of 5 to 35  $\mu\text{m}$  and having a shape not including cutting edges, and optionally, having an  $\alpha$ -ray radiant quantity smaller than 0.01  $\text{C}/\text{cm}^2 \cdot \text{hr}$ , and (2) a process for the preparation of  
10 spherical corundum particles as mentioned above, which comprises adding at least one member selected from the group consisting of halogen compounds, boron compounds, and alumina hydrates to a pulverization product of at least one member selected from the group consisting of  
15 electrofused alumina and sintered alumina, which has a specific particle size, heat-treating the mixture at a temperature of at least 1000°C, preferably 1000 to 1550°C, and disintegrating the heat-treated product.

Furthermore, in accordance with the present  
20 invention, there is provided (3) a rubber or plastic composition having a high thermal conductivity comprising spherical corundum particles having a maximum particle size smaller than 150  $\mu\text{m}$  and an average particle size of at least 10  $\mu\text{m}$  as single particles, and a shape not including cutting edges. In accordance with a preferred embodiment of the present invention, whereby an excellent effect of reducing burrs is realized at the step of molding a sealing material for a semiconductor, there is provided (4) a rubber or plastic composition  
25 having a high thermal conductivity which comprises alumina consisting of 1 to 20% by weight of fine alumina particles having an average particle size smaller than 5  $\mu\text{m}$ , the remainder of the alumina consisting of spherical corundum particles having a maximum size of a single  
30 particle that is smaller than 150  $\mu\text{m}$ , an average particle size of at least 10  $\mu\text{m}$ , and a shape not including cutting edges. Moreover, in accordance with another

preferred embodiment of the present invention, whereby an excellent effect of reducing the viscosity of a composition is realized upon incorporation in a liquid rubber or plastic, there is provided (5) a composition 5 having a high thermal conductivity and comprising at least one member selected from rubbers and plastics and, incorporated therein, at least 75% by weight, based on the total composition, of alumina consisting of 10 to 30% by weight of fine alumina particles having an 10 average particle size smaller than 5  $\mu\text{m}$ , the remainder of the alumina consisting of spherical corundum particles having an average particle size of at least 10  $\mu\text{m}$  and a shape not including cutting edges.

#### BRIEF DESCRIPTION OF THE DRAWINGS

15. Figure 1A, 1B, 2A, and 2B are scanning electron microscopes (2500 magnifications) of corundum particles, in which Fig. 1A shows corundum particles obtained in Example 1, Fig. 1B shows corundum particles obtained in Example 2, Fig. 1C shows corundum particles obtained in 20 Comparative Example 1 and Fig. 2B shows corundum particles obtained in Comparative Example 2.

#### BEST MODE FOR CARRYING OUT THE INVENTION

It was noted that a pulverized product of electro-fused alumina or sintered alumina, which has been used 25 as an abrasive material or a fine aggregate of a refractory material, having an average particle size of 5 to 35  $\mu\text{m}$ , preferably 10 to 25  $\mu\text{m}$  (for example, RW 220F or SRW 325F supplied by Showa Denko) has a particle size distribution which is substantially the same as the 30 particle size distribution of a pulverization product of fused silica or crystalline silica ( $\alpha\text{-SiO}_2$ ) used at present as a filler of a sealing material for an electronic part. Since such alumina has been molten or heat-treated at a high temperature such as 1500 to 35 1850°C, the crystal of alumina is fully developed and the pulverized product has a particle size distribution desirable for a filler. However, since sharp cutting

edges are formed at the pulverizing step as mentioned above, the pulverized product is not put to practical use as a filler. Accordingly, research was made with a view to improving the shape of the particles while 5 retaining this preferred particle size distribution, and as a result, it was found that, if a small amount of a known chemical heretofore used as a mineralizing agent or crystal-growing agent for alumina, such as a halogen compound or a boron compound, is incorporated into a 10 pulverized product of electrofused alumina or sintered alumina, and the mixture is heat-treated at a temperature of at least 1000°C, sharp angles, that is, cutting edges, of coarse particles of alumina are decreased and simultaneously, the shape is made 15 spherical. The present invention was completed based on this finding.

Electrofused alumina or sintered alumina prepared according to a known process can be used as starting coarse particles of alumina in the present invention. 20 The particle size distribution, determined according to the sedimentation method, of the pulverized product of electrofused or sintered alumina is such that the average particle size is 5 to 35  $\mu\text{m}$ , preferably 10 to 25  $\mu\text{m}$ , and the maximum particle size is not larger than 25 150  $\mu\text{m}$ , preferably not larger than 74  $\mu\text{m}$ . Where the average particle size of intended spherical corundum particles is smaller than 5  $\mu\text{m}$ , since particles having a rounded shape can be obtained by a known process comprising adding a crystal-growing agent to aluminum 30 hydroxide, the present invention need not be applied. If the average particle size of the starting material exceeds 35  $\mu\text{m}$  or the proportion of particles having a size larger than 150  $\mu\text{m}$  is increased, the effect of reducing cutting edges of the coarse particles is 35 insufficient and good results cannot be obtained. It was found that; if an alumina hydrate, especially aluminum hydroxide or alumina gel, or finely divided

alumina having a good thermal reactivity is added to electrofused alumina or sintered alumina and the mixture is heat-treated, the sphericalizing of coarse particles is effectively promoted. From the economical viewpoint, 5 aluminum hydroxide according to the Bayer process (gibbsite crystal) is preferred, and most preferably, the average particle size is smaller than 10  $\mu\text{m}$ . By observation, it was surprisingly confirmed that this sphericalizing promoter acts synergistically on coarse 10 particles of alumina, with chemicals described herein-after, and irregular and sharp cutting edges are selectively absorbed to sphericalize the coarse particles. As a subsidiary effect, the cohesive force of agglomerates of the heat-treated product is decreased 15 if an alumina hydrate such as aluminum hydroxide or alumina gel is added, and as a result, disintegration into primary particles can be easily accomplished. The optimum amount added of the sphericalizing promoting agent depends on the particle size of the pulverized 20 product of electrofused alumina or sintered alumina, but in the case of aluminum hydroxide, preferably the amount added of aluminum hydroxide is 5 to 100% by weight (calculated as alumina) based on electrofused alumina or sintered alumina. If the amount of aluminum hydroxide 25 is smaller than 5% by weight, the cohesive force of the agglomerates becomes strong, and if the amount of aluminum hydroxide exceeds 100% by weight, excessive aluminum hydroxide is included in the form of free fine particles of alumina in the product and good results 30 cannot be obtained.

At least one member selected from known crystal-growing agents for alumina is used as the chemical added at the heat treatment. Namely, halogen compounds, especially fluorine compounds such as  $\text{AlF}_3$ ,  $\text{NaF}$ ,  $\text{CaF}_2$ , 35  $\text{MgF}_2$ , and  $\text{Na}_3\text{AlF}_6$ , and/or boron compounds such as  $\text{B}_2\text{O}_3$ ,  $\text{H}_3\text{BO}_3$ , and  $\text{mNa}_2\text{O}\cdot\text{nB}_2\text{O}_3$  are preferred, and a mixture of a fluoride and a boron compound and a boro-

fluoride compound is particularly preferred. The amount added of the chemical depends on the heating temperature, the residence time in the furnace, and the kind of heating furnace, but it was found that a good effect is attained if the chemical is added in an amount of 0.1 to 4.0% by weight based on the total alumina. Known means such as a single furnace, a tunnel furnace, and a rotary kiln can be used as the heating furnace. Where an alumina hydrate such as aluminum hydroxide is made present together with the chemical, the heating temperature should be higher than the temperature at which the alumina hydrate is substantially converted to  $\alpha$ -alumina, that is, about 1150°C, and if the alumina hydrate is not made present, the intended object of the present invention can be attained by a heating temperature higher than 1000°C. In each case, a preferred heating temperature is in the range of 1350 to 1550°C. When the heating temperature is higher than 1550°C, even if aluminum hydroxide is present, the cohesive force of the agglomerates is increased and disintegration to primary particles cannot be easily accomplished. The residence time in the heating furnace depends on the heating temperature, but in order to sphericalize the particles, a residence time of at least 30 minutes is necessary. The spherical alumina particles prepared according to the above-mentioned process take the form of secondary agglomerated particles, and therefore, disintegration is carried out in a short time by using a known pulverizing means such as a ball mill, a shaking mill or a jet mill, whereby spherical corundum particles having a desired particle size distribution can be obtained.

If electrofused alumina or sintered alumina and aluminum hydroxide having a low content of a radioactive element such as uranium or thorium are used; spherical corundum particles having a small  $\alpha$ -ray radiant quantity can be prepared. If spherical alumina having a small

$\alpha$ -ray quantity (less than 0.01 C/cm<sup>2</sup>·hr) is used as a filler of a sealing resin for highly integrated IC, LSI and VLSI, a greater effect of preventing an erroneous operation (so-called soft error) by  $\alpha$ -rays can be attained.

The process for the preparation of the above-mentioned spherical corundum particles will now be summarized. The process comprises the steps of (1) using electrofused alumina or sintered alumina having an average particle size of 5 to 35  $\mu\text{m}$ , preferably 10 to 25  $\mu\text{m}$ , as the starting material, or optionally, a mixture of said alumina with fine particles of aluminum hydroxide in an amount of 5 to 100% by weight based on said alumina as the starting material, (2) adding 0.1 to 4.0% by weight of a halogen compound, especially a fluorine compound such as  $\text{CaF}_2$  or  $\text{AlF}_3$ , a boron compound such as  $\text{B}_2\text{O}_3$  or  $\text{H}_3\text{BO}_3$ , a combination of a fluorine compound and a boron compound, or a borofluoride such as  $\text{NH}_4\text{BF}_4$  to the starting material, (3) calcining the mixture at a temperature of at least 1000°C, preferably 1350 to 1550°C, and (4) lightly disintegrating the calcination product to single particles of  $\alpha$ -alumina (corundum).

If necessary, a step (5) of removing coarse particles (having a particle size exceeding 150  $\mu\text{m}$ ) by sieving may be optionally set. If the product is used in the field where a high hydrothermal resistance is required, for example, as an epoxy resin sealing material, a step (6) of refining the product by pickling or washing with deionized water becomes indispensable.

The spherical corundum particles prepared according to the above-mentioned process is valuable as a starting material of a finish wrapping material or as a base material of a refractory, glass or ceramics or a composite material thereof, but these spherical corundum particles are especially valuable as a filler of a composite material for an electronic part-mounting

material or electronic part-sealing material.

The spherical corundum of the present invention consists of single particles of corundum and is characteristic over spherical alumina formed by the flame-spray-  
5 ing method or plasma-jet method, which is a mixed crystal of  $\alpha$ -alumina and  $\delta$ -alumina and is composed of fine agglomerated particles. For this reason, the spherical corundum of the present invention is especially suitable as a filler for rubbers and plastics having  
10 a high thermal conductivity.

As the polymer in which the spherical corundum particles are to be incorporated, there can be mentioned thermoplastic engineering plastics such as polyethylene, polypropylene, nylons, polycarbonates, and polyphenylene sulfide, thermosetting plastics such as epoxy resins, unsaturated polyester resins, and phenolic resins, and elastomers such as silicone rubbers. Epoxy resins used for sealing IC's and LSI's, such as phenol-novolak resins and novolak-epoxy resins, silicone resins, and  
15 silicone rubbers for heat sinks, are preferred as the polymer. The amount filled of the spherical corundum particles varies according to the use, but when the spherical corundum particles are used as a composition with a powdery resin for a semiconductor chip-mounting  
20 material, preferably the spherical corundum particles are filled in an amount of 80 to 92% by weight. If the amount filled of the spherical corundum particles is smaller than 80% by weight, a thermal conductivity  
25 higher than  $60 \times 10^{-4}$  cal/cm $\cdot$ sec $\cdot$ °C cannot be obtained, and if the amount filled of the spherical corundum particles exceeds 92% by weight, the plastic flowability of the composition becomes insufficient and molding is difficult.

In this case, the maximum particle size of the  
35 spherical corundum particles is 150  $\mu\text{m}$ , and if particles having a size larger than this upper limit are incorporated, when the particles are filled in a rubber or

plastic, the surface becomes rough and wear is increased, and good results cannot be obtained. There is a range of the average particle size suitable for attaining a good balance among the less abrasive property, the 5 filling property, and the flowability. If the average particle size is smaller than 5  $\mu\text{m}$ , the flowability is reduced, and if the average particle size exceeds 35  $\mu\text{m}$ , the wear becomes larger than in the case of crystalline silica. It is especially preferable that the average 10 particle size is from 10 to 25  $\mu\text{m}$ .

The method for molding the highly thermally conductive rubber or plastic composition of the present invention is not particularly critical and an appropriate method is selected according to the kind of rubber or 15 plastic. For example, known molding methods such as transfer molding, press molding, roll molding, and cast molding can be adopted.

However, when a semiconductor is sealed by transfer-molding using a compound formed by incorporating spherical alumina as described above, a resin burr is likely 20 to adhere to a lead frame acting as a lead terminal of an IC or a transistor, and the subsequent plating step is not easily performed or an operation of removing the burr must be additionally performed. This disadvantage 25 can be eliminated by adding finely divided alumina B to spherical corundum particles A to adjust the particle size distribution. Namely, this plastic composition comprises (1) alumina consisting of 1 to 20% by weight of finely divided alumina B having an average particle 30 size smaller than 5  $\mu\text{m}$ , the remainder of the alumina consisting of spherical corundum particles A having a maximum single particle size smaller than 150  $\mu\text{m}$ , an average particle size of at least 10  $\mu\text{m}$ , and a shape not including cutting edges, and (2) at least one member 35 selected from plastics used for semiconductor-sealing materials, such as epoxy resins and silicone resins.

The finely divided alumina B is incorporated in

spherical corundum particles A in this composition because, since the proportion of particles having medium and fine particles is increased, the formation of a burr by bleeding of the resin from the spherical corundum particles can be prevented. Moreover, the mixing ratio of finely divided alumina B is limited to the above-mentioned range because, if the amount of finely divided alumina B is smaller than 1% by weight, the effect of preventing the formation of a burr is insufficient, and if the amount of finely divided alumina B is larger than 20% by weight, the wear property is increased or the moldability is degraded. The particles size of spherical corundum particles A is not particularly critical. However, if particles having a maximum particle size larger than 150  $\mu\text{m}$  are present, since the hardness of alumina is high, even though it has a spherical shape, the abrasive property is increased and good results cannot be obtained. The average particle size of finely divided alumina B is limited to smaller than 5  $\mu\text{m}$  because the wearing property is increased in the case of alumina having an average particle size exceeding this limit.

As is apparent from the foregoing description, this resin composition having a high thermal conductivity is especially suitable for sealing semiconductors and is characterized by the alumina incorporated, and this alumina is incorporated in a main component of a semiconductor-sealing material, such as an epoxy resin represented by a cresol-novolak type epoxy resin or a phenolic resin represented by a novolak type phenolic resin, as in the conventional technique. A filler other than alumina, for example, crystalline silica, a flame retardant, a lubricant, a parting agent, a colorant, and a coupling agent can be added, so far as the intended object is attained.

According to another valuable application mode of the present invention, the spherical corundum is

incorporated in a liquid rubber or plastic. In this case, a rubber or plastic composition having a low viscosity and an excellent castability and roll processability can be obtained by using a mixture comprising 5 spherical corundum particles A of the present invention and finely divided alumina B, at a B/(A + B) ratio of from 0.10 to 0.30.

Namely, this rubber or plastic composition having a high thermal conductivity comprises (1) alumina consisting of 10 to 30% by weight of finely divided alumina having an average particle size smaller than 5  $\mu\text{m}$ , the remainder of the alumina consisting of spherical corundum particles having an average particle size of at least 10  $\mu\text{m}$ , and (2) at least one member selected from rubbers 15 and plastics, wherein the amount incorporated of the alumina is at least 75% by weight based on the total composition.

The spherical corundum particles A used in this composition have an average particle size of at least 20 10  $\mu\text{m}$ . If the average particle size is smaller than 10  $\mu\text{m}$ , the viscosity-reducing effect by the combined use of spherical corundum particles A with finely divided alumina B is insufficient and good results cannot be obtained. The process for the preparation of finely 25 divided alumina is not particularly critical, but finely divided alumina having an average particle size smaller than 5  $\mu\text{m}$  is used. This is because, if finely divided alumina having a larger average particle size is used, the viscosity of the composition is increased and a 30 satisfactory effect cannot be attained.

By using alumina consisting of spherical corundum particles and 10 to 30% by weight (based on the total alumina) of finely divided alumina B, even if the alumina is incorporated in an amount of at least 75% by 35 weight (based on the total composition), preferably at least 80% by weight, in a liquid rubber or plastic, an increase of the viscosity of the resin composition,

which results in a degradation of the operation adaptability, can be prevented, and a rubber or plastic composition having a desired high thermal conductivity can be obtained. If the amount of finely divided 5 alumina B is smaller than 10% by weight based on the total alumina, when the alumina is filled at a high ratio, the effect of reducing the viscosity of the liquid resin composition is insufficient, and if the amount of finely divided alumina B exceeds 30% by 10 weight, the abrasive property is increased or the moldability is degraded. If the amount incorporated of the alumina is smaller than 75% by weight, a desired high thermal conductivity cannot be attained.

The kind of liquid rubber or plastic is not particularly critical, but epoxy resins, unsaturated polyester resins, phenolic resins, silicone resins, and silicone rubbers are preferred. A flame retardant, a colorant, a lubricant, a precipitation-preventing agent, a defoamer, and other fillers may be optionally added to the composition, so far as the intended object of the present 20 invention is attained.

The present invention will now be described with reference to the following examples.

Example 1

25 To 1000 g of commercially available pulverized sintered alumina (SRW-325F supplied by Showa Denko; average particle size = 12  $\mu\text{m}$ , maximum particle size = 48  $\mu\text{m}$ ) were added 20 g of anhydrous aluminum fluoride of the reagent class and 20 g of boric acid of the reagent 30 class. The mixture was charged in a heat-resistant vessel formed of an alumina ceramic and heated at 1450°C for 3 hours in a kanthal electric furnace. The hardness of agglomerates was determined with respect to the withdrawn calcination product. The calcination product 35 was disintegrated for 30 minutes in a vibration ball mill (SM-0.6 supplied by Kawasaki Jukogyo; 100 g of the calcination product and 1000 g of HD alumina balls

having a diameter of 10 mm were charged). The  $\text{Na}_2\text{O}$  content of the disintegration product was determined and the particle size distribution was determined by a laser diffraction technique (Cilas), and a scanning electron microscope photograph (2500 magnifications) was taken. The results are shown in the Example 1 Column in Table 1 and Fig. 1A.

Example 2

A calcination product and a disintegration product thereof were prepared by using commercially available pulverized electrofused alumina RW-92(325F) supplied by Showa Denko; average particle size =  $13 \mu\text{m}$ . The additives, the amounts incorporated, and the preparation method were the same as described in Example 1. The hardness of agglomerates of the calcination product, the total  $\text{Na}_2\text{O}$  content of the disintegration product, the particle size distribution, and the shape of  $\alpha$ -alumina particles were determined in the same manner as described in Example 1. The results are shown in the Example 2 Column in Table 1 and Fig. 1B.

Comparative Example 1

The same pulverized sintered alumina as used in Example 1 was heat-treated alone under the same conditions as described in Example 1, without the addition of the chemicals, and a calcination product and the disintegration product thereof were obtained. These samples were evaluated in the same manner as described in Example 1. The results are shown in the Comparative Example 1 Column in Table 1 and Fig. 2A.

Comparative Example 2

The same pulverized electrofused alumina as used in Example 2 was heat-treated alone under the same conditions as described in Example 2, without the addition of the chemicals, and the obtained calcination product and disintegration product were evaluated. The results are shown in the Comparative Example 2 Column in Table 1

and Fig. 2B.

From these results, it is seen that, in the corundum particles of the present invention (Examples 1 and 2), the average particle size was 16.0  $\mu\text{m}$  and the maximum 5 particle size was 50  $\mu\text{m}$  (Table 1), and as shown in Figs. 1A and 1B, the corundum particles had a rounded spherical shape having a size of 5 to 50  $\mu\text{m}$ . On the other hand, no change of the shape was caused by the heat treatment in the samples of Comparative Examples 1 10 and 2, and it was confirmed that the particles had an irregular shape including sharp cutting edges.

Table 1

Starting Material	Example 1	Example 2	Comparative Example 1	Comparative Example 2
	SRW(325F)	RW-92 (325F)	SRW(325F)	RW-92 (325F)
Crystal-Growing Agent	AlF <sub>3</sub> 2%	Same as in Example 1	not added	not added
	H <sub>3</sub> BO <sub>3</sub> 2%	Same as in Example 1		
Heating Conditions		1450°C x 3 hours		
Hardness of Agglomerates		Slightly hard	Slightly hard	Slightly hard
Analysis	total sodium content (Na <sub>2</sub> O) %	0.01	0.01	0.07
Volumes *1	particle size distribution *2			
	+32 microns (%)	9	12	6
	-10 microns (%)	25	20	45
	average particle size (microns)	16.0	18.5	12.0
α-alumina particles *3				
Size	5 - 50 microns	same as in Example 1	1 - 50 microns	same as in Comparative Example 1
Shape	spherical	spherical	irregular	irregular

Note

- \*1: analysis value obtained with respect to the sample disintegrated for 30 minutes by a vibration pot mill.
- \*2: determined according to the laser diffraction method (Cilas)
- \*3: determined by a scanning electron microscope.

From the results of the Examples and Comparative Examples, it is understood that the particles according to the present invention are quite different from the conventional particles having an irregular shape including sharp cutting edges, and are spherical corundum particles having a uniform shape and free of cutting edges.

Example 3

The same sintered alumina as used in Example 1 was mixed with 10% by weight (exteriorly calculated as alumina) of finely divided aluminum hydroxide having an average diameter of 1  $\mu\text{m}$ , and the same chemicals as used in Example 1 were added in the same amounts as in Example 1. The mixture was calcined and disintegrated in the same manner as described in Example 1. The obtained sample was evaluated in the same manner as described in Example 1. The results are shown in the Example 3 Column in Table 2.

Example 4

The evaluation results of a sample obtained in the same manner as described in Example 3, except that the amount added of aluminum hydroxide was changed to 17% by weight, are shown in the Example 4 Column in Table 2.

Example 5

The evaluation results of a sample obtained in the same manner as described in Example 3, except that the amount added of aluminum hydroxide was changed to 30% by weight, are shown in the Example 5 Column in Table 2.

Comparative Example 3

ball mill and passed through a sieve (Tyler sieve; mesh size = 104 microns). The residue on the sieve was removed. The alumina was mixed with 30% by weight of aluminum hydroxide having an average particle size of 5 about 5  $\mu\text{m}$  and with 2.0% by weight of anhydrous aluminum fluoride and 2.0% by weight of boric acid as the chemicals. The mixture was calcined and disintegrated in the same manner as described in Example 1. The evaluation results of the obtained sample are shown the 10 Example 7 Column in Table 3.

Example 8

Commercially available electrofused alumina [RW-92(220F) supplied by Showa Denko; average particle size = 28.5  $\mu\text{m}$ , maximum particle size = 196  $\mu\text{m}$ ] was 15 passed through a 150-mesh sieve, and the particles which had passed through the sieve were evaluated in the same manner as described in Example 7. The evaluation results are shown in the Example 8 Column in Table 3.

For comparison, the sample formed without the 20 addition of aluminum hydroxide was similarly tested (the results are not shown).

Where the procedures of Examples 7 and 8 were repeated without the addition of aluminum hydroxide, the particles of the calcination product were bonded to one 25 another in the semi-fused state, and disintegration by the mill was difficult. However, where aluminum hydroxide was incorporated, the calcination product could be easily disintegrated into primary particles.

Table 2

	Example 3	Example 4	Example 5	Comparative Example 3
Starting Material				
SRW 325F (wt. %)	100	100	100	100
aluminum hydroxide (wt. %)	10	17	30	30
Crystal-Growing Agents				
$\text{AlF}_3$ 2%	$\text{AlF}_3$ 2%	$\text{AlF}_3$ 2%	$\text{AlF}_3$ 2%	not added
$\text{H}_3\text{BO}_3$ 2%	$\text{H}_3\text{BO}_3$ 2%	$\text{H}_3\text{BO}_3$ 2%	$\text{H}_3\text{BO}_3$ 2%	
Heating Conditions				
	1450°C x 3 hours			
Hardness of Agglomerates				
Analysis	total sodium content ( $\text{Na}_2\text{O}$ ) %	0.01	0.01	0.25
volumes	particle size distribution			
	+32 microns (%)	17	11	6
	-10 microns (%)	22	28	30
	average particle size (microns)	19.4	16.5	15.0
	$\alpha$ -alumina particles			
	Size (microns)	5 - 50	4 - 50	3 - 50
	Shape	spherical	spherical, partially fine particles	mixture of irregular particles and fine particles

Table 3

		<u>Example 7</u>	<u>Example 8</u>
Starting Material		pulverized SRW 48F *1	RW-92 (200F)
Aluminum Hydroxide (5 microns)		30%	30%
Crystal-Growing Agent	$\text{AlF}_3$	2%	same as in Example 7
	$\text{H}_3\text{BO}_3$	2%	same as in Example 7
Heating Conditions		1450°C x 3 hours	
Hardness of Calcination Product		very soft	very soft
Analysis Values	total sodium content ( $\text{Na}_2\text{O}$ wt. %)	0.02	0.02
	particle size distribution		
	+32 microns (%)	26	35
	-10 microns (%)	12	15
	average particle size (microns)	21.7	25.6
	$\alpha$ -alumina particles		
	size	5 - 80 microns	5 - 80 microns
	shape	spherical	spherical

Note

\*1: sample obtained by pulverization for 1 hour by vibrating ball mill and passing through 150-mesh sieve (average particle size was 11 microns).

With respect to the samples of Examples 7 and 8, the measurement of the particle size distribution and the electron microscope observation were carried out. It was confirmed that each of the products of Examples 7 5 and 8 consisted of spherical coarse particles of  $\alpha$ -alumina particles having a particle size of 5 to 80 microns.

Example 9

Commercially available low- $\alpha$ -ray-radiant alumina 10 (having an  $\alpha$ -ray radiant quantity smaller than 0.01  $\text{C}/\text{cm}^2 \cdot \text{hr}$ ) was electrofused, and the obtained ingot was disintegrated, pulverized and classified under conditions such that a radioactive element was not included. The obtained electrofused alumina coarse particles 15 having an average particle size of 20 microns and a maximum particle size of 74 microns (the  $\alpha$ -ray radiant quantity was 0.005  $\text{C}/\text{cm}^2 \cdot \text{hr}$ ) were mixed with 30% by weight of aluminum hydroxide (average particle size of 5 microns) of the low  $\alpha$ -ray-radiant type ( $\alpha$ -ray radiant 20 quantity was 0.005  $\text{C}/\text{cm}^2 \cdot \text{hr}$ ) obtained according to the known method, and 0.5% by weight of boric acid and 0.5% by weight of anhydrous aluminum fluoride were added as the chemical. The mixture was charged in a heat-resistant vessel formed of an alumina ceramic and heated 25 at 1500°C for 3 hours in a kanthal electric furnace. The calcination product was pulverized for about 30 minutes by a vibration ball mill. The particle size distribution was determined and the size and shape of the particles were evaluated by an electron microscope. 30 It was confirmed that the starting particles were changed to spherical coarse  $\alpha$ -alumina particles having a particle size of 3 to 50 microns. The  $\alpha$ -ray radiant quantity of the sample was 0.004  $\text{C}/\text{cm}^2 \cdot \text{hr}$ .

Example 10

35 A basic recipe shown in Table 4 was set by using as the main component an epoxy resin for a sealing material for semiconductors.

Table 4

Materials	Amounts (parts by weight)
epoxy resin *1	100
phenolic resin *2	50
curing promoter *3	1
carnauba wax *4	3
alumina	variable

Note

- \*1: Sumiepoxy ESCN-220F (softening point = 77.6°C) supplied by Sumitomo Chemical K.K.
- \*2: Sumilite Resin PR-51688 (softening point = 98°C) supplied by Sumitomo Durez Co.
- \*3: Imidazole C-17Z supplied by Shikoku Kasei Kogyo K.K.
- \*4: supplied by Toa Chemical Industries Co., Ltd.

A composition comprising 650 parts (80.8% by weight), 850 parts (84.7% by weight) or 950 parts (86.0% by weight) of spherical corundum particles having the characteristics shown in Table 5 and prepared in Example 25 7 was kneaded for 3 minutes by two rolls having a surface temperature maintained at 105 to 115°C. After cooling, the product mass was disintegrated in a mortar and classified to a size smaller than 16 mesh. Tablets having a diameter of 50 mm were formed. With respect to 30 each of the above-mentioned three compositions, the spiral flow (flow characteristic of the composition) and the thermal conductivity and thermal expansion coefficient of a test piece obtained by press molding were determined. The thermal conductivity was measured by 35 the non-stationary hot wire method by using Shorthrerm<sup>®</sup> QTM-D II supplied by Showa Denko, the thermal expansion coefficient was expressed by the thermal expansion

coefficient  $\alpha_1$  at temperatures lower than the glass transition temperature, and the thermal expansion coefficient  $\alpha_2$  at temperatures higher than the glass transition temperature.

5        The spiral flow test was carried out according to EMMI-I-66 in the following manner. Namely, a spiral cavity mold was heated at  $149 \pm 3^\circ\text{C}$  and the sample was collected in an amount such that the cull thickness was 0.30 to 0.35 cm, and molding was carried out under a 10 pressure of  $70 \pm 2 \text{ kg/cm}^2$ . The distance which the sample moved along the spiral groove in the mold was measured. The result of the spiral test indicates the flowability of the sample and is important as a factor for evaluating the moldability.

15       In order to evaluate the abrasive property of the filler at the roll kneading step, the degree of contamination of the composition by wear of the hard chromium plating formed on the roll surface was judged with the naked eye. Namely, the degree of incorporation of a 20 peeled piece (black) of the hard chromium plating in the composition (white) by friction between alumina and the roll surface was evaluated with the naked eye according to the following five stages: 1) no contamination, 2) faint contamination, 3) little contamination, 4) conspicuous contamination and 5) extreme contamination, and 25 the degree of wear was determined by this contamination degree.

30       Note, in Table 5, the extraction impurities were measured by the pressure cooker test ( $160^\circ\text{C} \times 20$  hours). The pH value shown was the pH value of the supernatant of a slurry containing 30% by weight of the sample. The loose bulk specific gravity was measured by allowing the sample to fall naturally in a graduated cylinder, and the heavily packed bulk specific gravity was measured by 35 the tapping filling method. Furthermore, the average particle size was measured by the laser beam diffraction method (Cilas).

Table 5

Characteristics	Sample	Spherical Corundum (Example)	Coarse Alumina (Comparative Example)
moisture	(%)	0.01	0.02
ignition loss	(%)	0.02	0.05
Fe <sub>2</sub> O <sub>3</sub>	(%)	0.02	0.09
SiO <sub>2</sub>	(%)	0.13	0.06
Na <sub>2</sub> O	(%)	0.02	0.20
extraction impurities			
Na <sup>+</sup> ion	(ppm)	15.0	50.0
Cl <sup>-</sup> ion	(ppm)	0.4	2.0
extracted water electric conductivity	(mS/cm)	30	60
pH	(30% by weight)	5.5	6.0
bulk density gravity (g/cm <sup>3</sup> )			
loose		1.70	1.60
packed		2.40	2.20
average particle size (μm)		21.7	10.0
BET (specific surface area) (m <sup>2</sup> /g)		0.35	0.75

Comparative Example 4

A composition comprising 350 parts (70% by weight) of crystalline silica (Crystalite A-1 supplied by K.K. Tatsumori) having an average particle size of 9.7 μm and 30 a maximum particle size of 48 μm or fused silica (FuseLex E-1 supplied by K.K. Tatsumori) having an average particle size of 12.1 μm and a maximum particle size of 48 μm instead of spherical corundum was prepared in the same manner as described in Example 10, and the compo-

sition was evaluated in the same manner as described in Example 10.

Comparative Example 5

A composition comprising 650 parts of a sample  
5 formed by refining pulverized low-sodium alumina of the  
Bayer process (plate-like particles having an average  
size of 5  $\mu\text{m}$ ) by washing with pure water or a sample  
("Coarse Alumina" in Table 5) obtained by purifying  
commercially available sintered alumina (SRW 325F  
10 supplied by Showa Denko) having an average particle size  
of 10.0  $\mu\text{m}$  by washing with pure water, instead of the  
spherical corundum, was prepared in the same manner as  
in Example 10, and the characteristics were evaluated as  
in Example 10.  
15 The results obtained in Example 10 and Comparative  
Examples 4 and 5 are shown in Table 6.

Table 6

Kind of Alumina Filler	spherical corundum alumina by Bayer process	Example 10		Comparative Example 4		Comparative Example 5	
		650	850	950	650	650	650
	sintered alumina						
Silica	fused silica	350					
	crystalline silica		350				
Characteristics of Composition	wearing index	2	3	3	1	3	4
	spiral flow length (cm)	65	45	37	47	95	20
	thermal conductivity ( $\times 10^{-4}$ cal/cm.sec. $^{\circ}$ C)	62	75	84	16	34	55
	thermal expansion coefficient $\alpha_1$ ( $\times 10^{-5}/^{\circ}$ C)	2.2	1.9	1.8	1.9	3.4	1.9
	thermal expansion coefficient $\alpha_2$ ( $\times 10^{-5}/^{\circ}$ C)	6.6	6.0	5.8	5.6	8.1	5.8
	glass transition temperature ( $^{\circ}$ C)	179	175	173	178	173	172

As is apparent from the foregoing results, the spherical corundum of the present invention can be easily filled in a resin even at a weight ratio higher than 80% by weight, the wear by the spherical corundum of the present invention is much lower than that of crystalline silica, alumina by the Bayer process and sintered alumina, and the flowability represented by the spiral flow length is greatly improved. Accordingly, a thermal conductivity higher than  $60 \times 10^{-4}$  cal/cm·sec·°C can be easily obtained, and by increasing the amount incorporated of the spherical corundum, a low thermal expansion coefficient comparable to that of the fused silica-containing composition can be obtained.

Example 11

A composition was prepared by using an epoxy resin having a softening point of 68.6°C (Smiepoxy ESCN-220-3 supplied by Sumitomo Chemical K.K.) instead of the epoxy resin used in Example 10, changing the phenolic resin used as the curing agent in Example 10 to a phenolic resin having a softening point of 79°C (Shonol BRG-556 supplied by Showa Highpolymer Co., Ltd.) and incorporating 1050 parts (87.5% by weight) of spherical corundum shown in Table 5 without changing the amounts of other additives used in Example 10, and the characteristics of the composition were evaluated in the same manner as described in Example 10.

It was found that the wear index of the composition was 3, the spiral flow length was 40 cm, the thermal conductivity was  $93 \times 10^{-4}$  cal/cm·sec·°C, and the thermal expansion coefficient  $\alpha_1$  was  $1.7 \times 10^{-5}$  /°C.

Comparative Example 6

Spherical corundum purified products having average particle sizes of about 4  $\mu\text{m}$  and about 40  $\mu\text{m}$ , respectively, were prepared from sintered alumina finely divided into an average particle size of 3  $\mu\text{m}$  and sintered alumina having an average particle size of 37  $\mu\text{m}$ , respectively. It was intended to prepare com-

positions by using these spherical corundum purified products in the same manner as described in Example 11. In the case of alumina having an average particle size of 4  $\mu\text{m}$ , the composition became hard and roll kneading 5 was impossible. In the case of alumina having an average particle size of 40  $\mu\text{m}$ , kneading was relatively easy but the wear index was increased because the particle size was too large.

Examples 12 through 14 and Comparative Examples 7  
 10 through 11

Three kinds of alumina particles having characteristics shown in Table 7, that is, spherical alumina A, fine alumina B and medium alumina C, were mixed at a ratio shown in Table 8 to form a mixed filler. The 15 filler was incorporated in an amount shown in Table 9 into a resin to form a semiconductor-sealing resin composition.

With respect to the obtained material, the spiral flow length was measured according to the EMMI method, 20 and the length of the resin burr was measured. Moreover, in order to evaluate the wear property of the compound, the contamination of the compound with the hard chromium plating formed on the roll surface at the roll kneading step was judged with the naked eye and expressed by the index.

Table 7

	<u>Spherical<sup>1)</sup> Alumina A</u>	<u>Fine<sup>2)</sup> Alumina B</u>	<u>Medium<sup>3)</sup> Alumina C</u>
Average Particle Size	20	1.5	10
Maximum Particle Size	64	6	32
Shape	spherical	irregular	irregular

Note

- 1) spherical alumina
- 2) AL-45-1 supplied by Showa Denko K.K.
- 3) SRW 325F supplied by Showa Denko K.K.

Table 8

Mixing Ratio (%)	spherical alumina A <sup>1)</sup>	Example No.			Comparative Example No.				
		12	13	14	7	8	9	10	11
		99	90	80	100	70	50		80
	fine alumina B <sup>2)</sup>		1	10	20		30	50	100
	medium alumina C <sup>3)</sup>							20	

Table 9

Materials	Amounts (g)
Epoxy Resin 1)	100
Phenolic Resin 2)	50
Curing Promoter 3)	1
Mold Release 4)	3
Alumina	850

Note

- 1) ESCN-220-3 supplied by Sumitomo Chemical K.K.
- 2) BRG-556 supplied by Showa Highpolymer Co., Ltd.
- 3) C-17Z supplied by Shikoku Chemical K.K.
- 4) carnauba wax supplied by Hoechst

The length of the resin burr referred to herein means the length of a burr formed when the molding material was transfer-molded at a width of 10 mm and a slit thickness of 10, 30, 75 or 98  $\mu\text{m}$ . If the burr length is smaller than 10 mm at each slit thickness, no problem arises.

Table 10

Ratio	B/A + B	Example No.			Comparative Example No.				
		12	13	14	7	8	9	10	11
Characteristics	spiral flow length (cm) <sup>1)</sup>	55	60	62	52	55	35	29	38
	Wear index <sup>2)</sup>	2	2	2	2	3	4	5	5
burr strength (mm)	10 $\mu\text{m}$	4	2	2	11	2	7	30	20
	30 $\mu\text{m}$	6	3	3	25	8	10	45	26
	76 $\mu\text{m}$	8	4	4	38	10	15	50	41
	98 $\mu\text{m}$	10	5	5	45	15	20	50	50

Note

1)  $149 \pm 3^\circ\text{C}$ ,  $70 \pm 2 \text{ kg/cm}^2$

2) 1: no contamination

2: faint contamination

3: little contamination

4: conspicuous contamination

5: extreme contamination

As is apparent from the test results shown in Table 10, only in Examples 12 through 14 where the added alumina was fine alumina B and the mixing ratio was 0.01 to 0.20, was the wear property low, the formation of a resin burr controlled, and the flowability represented by the spiral flow length large.

In Comparative Examples 8 and 9, where even if the added alumina was alumina B, the ratio of the alumina B was outside the range specified in the present invention, the wear index was increased although formation of a burr was controlled to a certain extent. In Comparative Example 10, where all of the filled alumina was the fine alumina, wear was extreme, the flowability was reduced, the burr length was large, and a satisfactory material could not be obtained. In Comparative Example 11, where the added alumina was medium alumina having an average particle size exceeding 5 microns, the spiral flow length was short, wear was extreme, and the formation of burrs was not controlled.

Note, the thermal conductivities obtained in these examples were  $74$  to  $75 \times 10^{-4}$  cal/cm $\cdot$ sec $\cdot$ °C.

Examples 15 through 18 and Comparative Examples 12 through 17

The alumina shown in Table 11 was incorporated at a ratio shown in Table 12 into an epoxy resin to obtain a resin composition having a high thermal conductivity.

The mixing ratio of the alumina particles in the added alumina was as shown in Table 13. Note, alumina B, alumina C, and alumina D were according to the Bayer process.

Table 11  
Characteristics of Alumina

Items	Spherical	Fine	Medium	Medium	Sintered	Spherical
	Corundum	Alumina	Alumina	Alumina	Alumina	Corundum
	A	B	C	D	E	F
Average Particle Size ( $\mu\text{m}$ )	20	1	6	8	12	9
Maximum Particle Size ( $\mu\text{m}$ )	64	12	16	24	32	48

Table 12Mixing Ratio

<u>Material</u>	<u>Amount Incorporated</u>
Epoxy Resin <sup>1)</sup>	50 g
Curing Agent <sup>2)</sup>	40 g
Alumina	200 - 400 g

Note

- 1) Epikote 815 supplied by Shell Chemical
- 2) NH-2200 supplied by Hitachi Chemical Co., Ltd.

Table 13Composition (%) of Added Alumina

	<u>Example No.</u>				<u>Comparative Example No.</u>				
	<u>15</u>	<u>16</u>	<u>17</u>	<u>12</u>	<u>13</u>	<u>14</u>	<u>15</u>	<u>16</u>	<u>17</u>
Spherical Corundum A	90	80	70	100	60	80			
Fine Alumina B		10	20	30		40			20
Medium Alumina C						20			
Medium Alumina D							100		
Sintered Alumina E								100	
Spherical Corundum F									80

The viscosity of each of the so-obtained compounds was measured, and the results are shown in Table 14.

Table 14  
Viscosity (poise) of Compound

Amount (g) of Added Alumina	Example No.			Comparative Example No.					
	15	16	17	12	13	14	15	16	17
200	69	65	68	70	85	70	232	172	125
250	130	105	135	153	192	148	785	671	391
300	226	173	229	371	503	335	1920	2390	980
350	478	358	500	750	1020	721	above 3000	above 3000	1970
400	724	550	770	1300	1630	1250	above 3000	above 3000	above 3000

20 From the experimental results shown in Table 14, it is seen that, only when the fine alumina having an average particle size smaller than 5  $\mu\text{m}$  was incorporated in an amount of 10 to 30% by weight in spherical corundum, was the viscosity of the resulting compound low and the 25 compound had a good operation adaptability even if the alumina was added in a large amount. In Comparative Example 12, where spherical corundum alone was incorporated, or in Comparative Example 13, where the ratio of fine alumina to spherical corundum was outside the range 30 specified in the present invention, the viscosity was increased. In Comparative Example 14 where the average particle size of added fine alumina was larger than 5  $\mu\text{m}$ , even if the mixing ratio of the fine alumina was 10 to 30% by weight, when the alumina filler was 35 incorporated in a large amount, the viscosity was high and a compound having a good operation adaptability could not be obtained. Similarly, in Comparative

Example 15, where the particle size of the added alumina was relatively large, in Comparative Example 16, where the pulverized sintered alumina was incorporated, or in Comparative Example 17, where the average particle size 5 of spherical corundum particles was smaller than 10  $\mu\text{m}$ , a satisfactory compound was not obtained.

The alumina filler was gradually added to the resin, and when the viscosity of the compound reached 500 poise, the ratio of the alumina in the compound was 10 determined. The compound at this time was cured and the thermal conductivity was measured. The results are shown in Table 15.

Table 15

	Example No.				Comparative Example No.				
	15	16	17	12	13	14	15	16	17
Ratio (% by weight) of Alumina at which Viscosity Reached 500 poise	80	81	80	78	77	79	72	73	74
Thermal Conductivity $10^{-4}$ cal/cm $\cdot$ sec $\cdot$ °C	53	56	53	45	42	49	31	33	35

It is considered that the operation adaptability of a liquid compound is drastically degraded if the viscosity of the compound exceeds 500 poise. As is seen from Table 15, only in Examples 15 through 17 where spherical 30 corundum particles containing 10 to 30% by weight of fine alumina having an average particle size smaller than 5  $\mu\text{m}$  were incorporated, was the viscosity of the compound lower than 500 poise even if the alumina was incorporated in an amount of 80% or more, and a thermal conductivity 35 higher than  $50 \times 10^{-4}$  cal/cm $\cdot$ sec $\cdot$ °C obtained. On the other hand, where spherical corundum particles were used, the average particle size of the added alumina was

larger than 5  $\mu\text{m}$  or the average particle size of the added alumina was smaller than 5  $\mu\text{m}$ , the mixing ratio of the added alumina was outside the range of 10 to 30% by weight, as in Comparative Examples 12 through 14, or in 5 where pulverized sintered alumina having a relatively large particle size or spherical corundum having an average particle size smaller than 10  $\mu\text{m}$  was used, as in Comparative Examples 12 and 15 through 17, the viscosity reached 500 poise when the amount added of the alumina 10 was still small, and therefore, a compound providing a high thermal conductivity could not be obtained.

#### INDUSTRIAL APPLICABILITY

The spherical corundum of the present invention has a low abrasive property and excellent flow characteristics and is valuable as a filler for a sealing material for electronic parts, a starting material of a finish wrapping material, a base material of a refractory, glass or ceramic. Moreover, a rubber or plastic composition comprising a high concentration of this 20 spherical corundum has a high thermal conductivity and a low thermal expansion coefficient, and therefore, this composition is especially valuable as an insulating sealing material for a semiconductor device.

CLAIMS

1. Spherical corundum particles characterized by consisting substantially of single particles, having an average particle size of 5 to 35  $\mu\text{m}$  and having a shape not including cutting edges.
- 5 2. Spherical corundum particles characterized by having a maximum particle size smaller than 150  $\mu\text{m}$  and an average particle size of 5 to 35  $\mu\text{m}$  as single particles, having a shape not including cutting edges, and having an  $\alpha$ -ray radiant quantity smaller than 0.01  $\text{C}/\text{cm}^2 \cdot \text{hr.}$
- 10 3. A process for the preparation of spherical corundum particles, characterized by adding one or more members selected from the group consisting of halogen compounds, boron compounds and alumina hydrates to a pulverized product of at least one member of electro-fused alumina and sintered alumina, which has a maximum particle size smaller than 150  $\mu\text{m}$  and an average particles size of 5 to 35  $\mu\text{m}$  as single particles, heat-treating the mixture at a temperature of at least 1000°C, and disintegrating the heat-treated product.
- 15 4. A process for the preparation of spherical corundum particles according to claim 3, wherein the heat treatment is carried out at 1000 to 1550°C.
- 20 5. A process for the preparation of spherical corundum particles according to claim 3, wherein the halogen compound is one or more members selected from the group consisting of  $\text{AlF}_3$ ,  $\text{NaF}$ ,  $\text{CaF}_2$ ,  $\text{MgF}_2$  and  $\text{Na}_3\text{AlF}_6$ .
- 25 6. A process for the preparation of spherical corundum particles according to claim 3, wherein the boron compound is one or more members selected from the group consisting of  $\text{B}_2\text{O}_3$ ,  $\text{H}_3\text{BO}_3$ ,  $\text{mNa}_2\text{O} \cdot \text{nB}_2\text{O}_3$  and borofluorides.
- 30 7. A process for the preparation of spherical corundum particles according to claim 3, wherein the alumina hydrate is at least an aluminum hydroxide
- 35

produced by the Bayer process and alumina gel.

8. A process for the preparation of spherical corundum particles according to claim 3, wherein each of electrofused alumina, sintered alumina and alumina hydrate has an  $\alpha$ -ray radiant quantity smaller than 5 0.01 C/cm<sup>2</sup>·hr.

9. Spherical corundum particles characterized by being formed by adding one or more members selected from the group consisting of halogen compounds, boron compounds and alumina hydrates to a pulverized product of at least one of electrofused alumina and sintered alumina, which has a maximum particle size smaller than 10 150  $\mu\text{m}$  and an average particle size of 5 to 35  $\mu\text{m}$  as single particles, heat-treating the mixture at a temperature of at least 1000°C, and disintegrating the 15 heat-treated product.

10. A highly thermally conductive composition comprising spherical corundum particles having an average particles size of 5 to 35  $\mu\text{m}$  and a shape not 20 including cutting edges, and at least one of rubbers and plastics.

11. A composition as set forth in claim 10, wherein the spherical corundum particles have an  $\alpha$ -ray radiant quantity smaller than 0.01 C/cm<sup>2</sup>·hr.

25 12. A composition as set forth in claim 10, wherein the spherical corundum particles are contained at a weight ratio of 80 to 92%.

13. A composition as set forth in claim 10, where 30 the spherical corundum particles have an average particle size of 10 to 25  $\mu\text{m}$ .

14. A composition as set forth in claim 10, wherein the plastic is selected from thermoplastic engineering plastics such as polypropylene, polyethylene, nylons, polycarbonates and polyphenylene sulfide, and 35 thermosetting plastics such as epoxy resins, unsaturated polyester resins and phenolic resins.

15. A composition as set forth in claim 10,

wherein the rubber is a silicone rubber.

16. A resin composition for sealing a semiconductor, characterized by comprising (1) alumina consisting of 1 to 20% by weight of finely divided alumina having an average particle size smaller than 5  $\mu\text{m}$ , the remainder of the alumina consisting of spherical corundum particles having a maximum particle size smaller than 150  $\mu\text{m}$  and an average particle size of at least 10  $\mu\text{m}$  as single particles and a shape not including cutting edges, and (2) at least one of plastics used for a semiconductor-sealing material, such as epoxy resins and silicone resins.

17. A composition characterized by comprising (1) alumina consisting of 10 to 30% by weight of finely divided alumina having an average particle size smaller than 5  $\mu\text{m}$ , the remainder of the alumina consisting of spherical corundum particles having an average particle size of at least 10  $\mu\text{m}$  and a shape not including cutting edges, and (2) at least one of rubbers and plastics, wherein the amount incorporated of the alumina is at least 75% by weight.

18. A composition as set forth in claim 10, wherein the spherical corundum particles having a maximum single particle diameter smaller than 150  $\mu\text{m}$  and an average particles of 5 to 35  $\mu\text{m}$  as single particles are those formed by adding at least one member of halogen compounds, boron compounds and alumina hydrates to a pulverized product of at least one of electrofused alumina and sintered alumina, which has a maximum single particle size smaller than 150  $\mu\text{m}$  and an average particle size of 5 to 35  $\mu\text{m}$ , heat-treating the mixture at a temperature of at least 1000°C, and disintegrating the heat-treated product.

19. A composition as set forth in claim 16 or 17, wherein the spherical corundum particles having a maximum particle size smaller than 150  $\mu\text{m}$  and an average particle size of at least 10  $\mu\text{m}$  as single particles are

those formed by adding at least one of halogen compounds, boron compounds and alumina hydrates to a pulverized product of at least one of electrofused alumina and sintered alumina, which has a maximum single particle 5 size smaller than 150  $\mu\text{m}$  and an average particle size of at least 10  $\mu\text{m}$ , heat-treating the mixture at a temperature of at least 1000°C, and disintegrating the heat-treated product.

20. An electronic part comprising (1) a semi-conductor chip for a power module, and (2) a mounting member for mounting thereby the semiconductor chip while having contact therewith, said mounting member being composed of a composition comprising spherical corundum particles having an average particle size of 5 to 35  $\mu\text{m}$  15 and a shape not including cutting edges and at least one of plastics and rubbers.

21. A semiconductor device comprising (1) a semiconductor chip, and (2) a mounting member for mounting thereby the semiconductor chip while having contact therewith, said mounting member being composed 20 of a composition comprising: alumina consisting of 1 to 20% by weight of finely divided alumina having an average particle size smaller than 5  $\mu\text{m}$ , the remainder of the alumina consisting of spherical corundum particles 25 having a maximum particle size smaller than 150  $\mu\text{m}$  and an average particle size of at least 10  $\mu\text{m}$  as single particles and a shape not including cutting edges; and at least one of rubbers and plastics.

22. An electronic part as set forth in claim 20 30 or 21, wherein the mounting member is an insulating sealing member for the semiconductor chip.

23. An electronic part as set forth in claim 20 or 21, wherein the mounting member is a circuit substrate on which the semiconductor chip is mounted.

1/1

Fig. 1A



Fig. 1B



Fig. 2A



Fig. 2B



## INTERNATIONAL SEARCH REPORT

International Application No PCT/JP87/00508

## I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all):

According to International Patent Classification (IPC) or to both National Classification and IPC  
 Int.Cl 4 C01F7/02, C08K7/18, H01L23/30,  
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## II. FIELDS SEARCHED

Minimum Documentation Searched 4

Classification System	Classification Symbols
IPC	C01F7/02, 7/44, 7/46, C08K7/16~28, H01L23/14, 23/30, H05K1/03

Documentation Searched other than Minimum Documentation  
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## III. DOCUMENTS CONSIDERED TO BE RELEVANT 14

Category 15	Citation of Document, 16 with indication, where appropriate, of the relevant passages 17	Relevant to Claim No. 18
A	JP, A, 59-97528 (Swiss Aluminium Ltd.) 5 June 1984 (05. 06. 84) & EP, B, 105025	1-9
A	JP, A, 58-181725 (Swiss Aluminium Ltd.) 24 October 1983 (24. 10. 83) & EP, B, 90767	3-9
A	JP, B, 60-26505 (Nippon Steel Corporation and one other) 24 June 1985 (24. 06. 85) (Family: none)	10-23
A	JP, A, 59-30719 (Sumitomo Chemical Co., Ltd.) 18 February 1984 (18. 02. 84) (Family: none)	2
E	JP, A, 62-191420 (Showa Kei Kinzoku Kabushiki Kaisha) 21 August 1987 (21. 08. 87) (Family: none)	1-11, 13-14, 18, 20, 22-23

## \* Special categories of cited documents 19

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- "Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "Z" document member of the same patent family

## IV. CERTIFICATION

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### ㉒ Resin composition.

㉓ A resin composition having inorganic filler particles with an average particle size of from 0.05 to 150  $\mu\text{m}$  incorporated in an amount of from 20 to 85% by volume based on the entire resin composition, wherein:

- (a) said particles comprise at least two groups of particles differing in the average particle size,
- (b) particles constituting a group of particles with the smallest average particle size, are spherical particles with an average particle size smaller than 5  $\mu\text{m}$ ,
- (c) a group or groups of particles with an average particle size larger than the particles of (b), are constituted by spherical particles, pulverized particles or a mixture thereof,
- (d) as between two groups of particles with their average particle sizes being close to each other, the ratio of the minimum particle size within a range defined by the standard deviation of the particle size distribution of the group of particles with a large average particle size, to the maximum particle size within a range defined by the standard deviation of the particle size distribution of the group of particles with a small average particle size, is at least 2, and
- (e) the proportion of the volume of the group of particles with a large average particle size, to the total volume of the two groups of particles with their average particle sizes being close to each other, is from 20 to 95% by volume.

EP 0 361 109 A1

## RESIN COMPOSITION

The present invention relates to a resin composition having an inorganic filler incorporated therein. More particularly, it relates to a resin composition having a large content of an inorganic filler and yet having excellent moldability and flowability.

It is known to incorporate various fillers for the purpose of reinforcing a resin or improving the properties of a resin. Such fillers include organic and inorganic materials. As a material containing a relatively large amount of an inorganic filler, there may be mentioned a filler for dental use or a sealant for semiconductors or for various electronics parts.

For example, IC (integrated circuit) and LSI (large scale integration) are sealed with a sealant to protect the semiconductor elements from external impacts, moisture, heat and  $\alpha$ -rays. As such a sealant, ceramics or a resin is mainly employed. Sealing with a resin (plastic sealing) is advantageous in that it is inexpensive and excellent for mass production. Plastic sealing by low pressure transfer molding by means of an epoxy resin having excellent air tight sealing properties and heat resistance, is particularly preferred and most commonly employed.

However, in such plastic sealing, due to a stress caused by the difference in the thermal expansion coefficient between the silicon chip and the resin, aluminum wirings or bonding wires are likely to deform or break, or cracking of passivation and sealant is likely to take place to cause a change in the electrical properties of the integrated circuit or a deterioration of the moisture resistance. In order to reduce such a stress, it has been proposed to incorporate an inorganic filler to the resin to reduce the difference in the thermal expansion coefficient from the silicon chip. To reduce the difference in the thermal expansion coefficient by the addition of an inorganic filler to the resin, the larger the amount of the filler, the better. However, as the amount of the filler increases, the melt viscosity of the resin composition increases, and flowability decreases, thus adversely affecting the moldability.

Under the circumstances, it has been desired to develop a material having a large amount of a filler incorporated to reduce the difference in the thermal expansion coefficient and yet having excellent moldability. Such a demand increases as the trend for high integration or for large size semiconductor chips progresses.

Heretofore, for resin compositions for sealing semiconductors, it has been proposed to use spherical silica as an inorganic filler (Nikkei New Materials, March 30, 1987, p. 32) or to use at least two types of silica differing in the particle size (e.g. Japanese Unexamined Patent Publication No. 34052/1986). However, neither one fully satisfies the above demand.

The present inventors have conducted extensive researches with an aim to develop a resin composition having an inorganic filler incorporated, whereby a large amount of the filler may be incorporated and yet excellent moldability is attainable. It has now been found possible to accomplish this object by using as a filler at least two groups of inorganic filler particles differing in the average particle size, comprising a group of fine spherical particles with an average particle size of at most 5  $\mu\text{m}$  and a group or groups of particles with larger particle sizes. Further, it has been found that the melt viscosity of the resin composition can further be improved by mixing the filler particles under certain specific conditions before incorporation.

The present invention provides a resin composition having inorganic filler particles with an average particle size of from 0.05 to 150  $\mu\text{m}$  incorporated in an amount of from 20 to 85% by volume based on the entire resin composition, wherein:

- (a) said particles comprise at least two groups of particles differing in the average particle size,
- (b) particles constituting a group of particles with the smallest average particle size, are spherical particles with an average particle size smaller than 5  $\mu\text{m}$ ,
- (c) a group or groups of particles with an average particle size larger than the particles of (b), are constituted by spherical particles, pulverized particles or a mixture thereof,
- (d) as between two groups of particles with their average particle sizes being close to each other, the ratio of the minimum particle size within a range defined by the standard deviation of the particle size distribution of the group of particles with a large average particle size, to the maximum particle size within a range defined by the standard deviation of the particle size distribution of the group of particles with a small average particle size, is at least 2, and
- (e) the proportion of the volume of the group of particles with a large average particle size, to the total volume of the two groups of particles with their average particle sizes being close to each other, is from 20 to 95% by volume.

The present invention is concerned also with a composition obtained by dispersing and mixing in a polar organic liquid the particles as defined by the above (a) to (e) and then incorporating them to a resin.

Now, the present invention will be described in detail with reference to the preferred embodiments.

The resin used in the resin composition of the present invention may be a thermoplastic resin or a curable resin which may be cured by heat, light or microwaves or by a chemical reaction, such as a thermosetting resin or a photocurable resin. As the curable resin, an epoxy resin, a bismaleimide resin, a 5 urea resin or an acrylate resin may be mentioned. Such a curable resin may contain a curing accelerator such as a photosensitizer, a reaction accelerator or a catalyst, or a pigment, a releasing agent, a flexibility-imparting agent or other additives. As the thermoplastic resin, a polyolefin such as polyethylene or polypropylene, a polystyrene, a polyamide, a polyethylene terephthalate, a polybutylene terephthalate, a 10 polyacetal, a polycarbonate, a polyallylate, a polysulfone, a polyethersulfone, a polyether ether ketone, a liquid crystalline polyester, a polyphenylene sulfide, a polyamideimide, a polyimide, a polyetherimide or a polymethyl methacrylate, may be mentioned. However, the useful thermoplastic resin is not restricted to such specific examples. Further, it may contain a pigment or other additives.

These resins may be used alone or in combination as a blend or a complex obtained by alloying two or more different kinds.

15 The inorganic filler particles to be used in the present invention include spherical particles and pulverized particles of e.g. silica, alumina, titania, zirconia, titanium silicate, aluminum silicate, lithium-aluminum silicate, magnesium-aluminum silicate, aluminum titanate, aluminum nitride and silicon nitride. However, the useful inorganic filler particles are not restricted to such specific examples. Further, two or more different types of fillers may be used in combination.

20 The resin and the filler are suitably selected depending upon the particular purpose of use and the desired properties. For example, for the purpose of a sealant for semiconductors, it is usual to employ an epoxy resin. Various known epoxy resins may be used. To the resin, various additives such as a curing agent, a curing accelerator, a pigment, a releasing agent or a flexibility-imparting agent may be incorporated.

25 The inorganic filler is incorporated for the purpose of reducing the thermal expansion coefficient of the resin. Therefore, it is preferably the one having a low thermal expansion coefficient itself. In this respect, silica is most preferred. Further, the inorganic filler is required to be of high purity without substantially containing impure elements such as chlorine, uranium or thorium, in order to prevent corrosion of aluminum wirings or software malfunction.

30 For the resin composition of the present invention, the inorganic filler particles with an average particle size within a range of from 0.05 to 150  $\mu\text{m}$  are employed. If the average particle size is smaller than 0.05  $\mu\text{m}$ , the specific surface area of the particles tends to be large, whereby coagulation is likely to result, and it tends to be difficult to obtain a resin composition having particles incorporated at a high density. On the other hand, if particles with an average particle size exceeding 150  $\mu\text{m}$  are employed, when particles with a 35 different particle size are mixed thereto and then the mixture is kneaded with a resin, followed by melt molding, such particles tend to be separated from the particles having the different particle size, whereby uniform mixing and uniform molding tend to be difficult.

The inorganic filler to be used in the present invention is required to satisfy the following conditions:

40 (a) the inorganic filler particles comprise at least two groups of particles differing in the average particle size;

(b) among such groups of particles, particles constituting a group of particles with the smallest average particle size are spherical particles with an average particle size smaller than 5  $\mu\text{m}$ , preferably at most 2  $\mu\text{m}$ , more preferably at most 1.0  $\mu\text{m}$ ;

45 (c) a group or groups of particles with an average particle size larger than the particles of (b) are constituted by spherical particles and/or pulverized particles;

(d) as between two groups of particles with their average particle sizes being close to each other, the ratio of the minimum particle size within a range defined by the standard deviation of the particle size distribution of the group of particles with a large average particle size, to the maximum particle size within a range defined by the standard deviation of the particle size distribution of the group of particles with a small average particle size, is at least 2, preferably at least 5; and

50 (e) the proportion of the volume of the group of particles with a large average particle size, to the total volume of the two groups of particles with their average particle sizes being close to each other, is from 20 to 95% by volume, more preferably from 50 to 90% by volume.

These conditions (a), (b), (c), (d) and (e) will be described in further detail.

55 The number of groups of particles differing in the average particle size is suitably selected taking into consideration the particle size distributions of the respective groups of particles or the particle size ratio among the groups of the particles.

The particles with an average particle size within a range of from 0.05 to 150  $\mu\text{m}$  as specified in the

present invention, may theoretically contain up to twelve groups of particles when the particle size ratio as between the two close groups of particles as specified in (d) is 2 and the particles of each group are assumed to have a uniform particle size (i.e. no particle size distribution). However, when each group of particles has a particle size distribution, for example, when the standard deviation ( $\sigma$ ) of the particle size distribution is 1.2, the particles as specified in the present invention may theoretically contain up to 8 groups of particles. When the standard deviation ( $\sigma$ ) of the particle size distribution is 1.2 and the particle size ratio is as specified in (d) is 5, the particles of the present invention may theoretically contain up to 4 groups of particles.

(b). The spherical particles with an average particle size smaller than 5  $\mu\text{m}$  as the group of particles with the smallest average particle size, are believed to be present in the spaces among particles of other larger particle sizes to increase the content of the filler and to serve as a lubricant to increase the slippage of the larger particles in the resin composition. However, if the average particle size of spherical particles exceeds 5  $\mu\text{m}$ , they tend to hardly enter into the spaces among large particles.

(c) As the group of particles with an average particle size larger than the particles of (b), spherical particles and pulverized particles may be used alone independently or in combination as a mixture. When it is desired to increase the filler content or the flowability of the resin composition, it is preferred to employ spherical particles. From the viewpoint of the costs, it is advantageous to use pulverized particles. Both types of particles may be used in combination. The blend ratio of the spherical particles and the pulverized particles may suitably be determined taking into consideration the properties and the cost of the resin composition.

(d) As between two groups of particles with their average particle sizes being close to each other, if the ratio of the minimum particle size within a range defined by the standard deviation of the particle size distribution of the group of particles with a large average particle size, to the maximum particle size within a range defined by the standard deviation of the particle size distribution of the group of particles with a small average particle size, is less than 2, small particles tend to hardly enter into spaces among large particles, such being undesirable.

(e) If the proportion of the volume of the group of particles with a large average particle size, to the total volume of the two groups of particles with their average particle sizes being close to each other, is less than 20% by volume, the filler content tends to be small in such a state that large particles are scattered in the small particles. On the other hand, if the volume of the group of particles with a large average particle size exceeds 95% by volume, the filler content tends to be small, since the proportion by volume of small particles filling the spaces among large particles tends to be small relative to the increase of the spaces among large particles.

In general, the particle size distribution of each group of particles is preferably narrow. For example, the standard deviation is preferably at most 2, more preferably at most 1.5, and most preferably at most 1.2. However, in the actual situation, it is unnecessary to closely follow such standard deviation.

Namely, when the particle size ratio as defined in (d) is considerably large i.e. when there is a substantial difference in the particle size between the major portions of the two groups of particles, small particles can adequately be packed in spaces among large particles even if the particle size distributions of the respective groups of particles are relatively broad, and no problem of void spaces will thereby be brought about. Accordingly, the particle distributions of the respective groups of particles may be selected suitably depending upon the particular case taking into consideration the particle size ratio as defined in (d).

When the inorganic filler satisfying the above conditions for the shapes of the particles, for the average particle sizes, for the particle size distributions, for the ratios of the average particle sizes of particles and for the proportions of the volumes of the groups of particles, is kneaded with a resin and other additives, particles with small average particle sizes will effectively be packed in spaces among particles with relatively large average particle sizes, whereby it is possible to increase the inorganic filler incorporated to the total resin composition while maintaining a high level of flowability.

In the resin composition of the present invention, the filler may be incorporated up to 85% by volume of the resin composition.

Even when the amount of the filler is small, it is possible to obtain a composition with the melt viscosity reduced over the resin composition containing the same amount of the filler obtained by the conventional method.

The incorporated amount is calculated by the following formula I:

$$\frac{\text{Incorporated amount (\%)} \times 100}{\text{W-particles/p-particles} + \text{W-resin/p-resin}} \quad \dots \quad (I)$$

5

W-particles: weight (g) of the incorporated filler

p-particles: density (g/cm<sup>3</sup>) of the filler

W-resin: weight (g) of the incorporated resin (including additives)

10 p-resin: density (g/cm<sup>3</sup>) of the resin (including additives)

For blending the inorganic filler to the resin, the inorganic filler and the resin, if necessary together with additives such as a curing agent or a pigment, are sufficiently uniformly mixed by e.g. a mixer, and melt-mixed by means of e.g. heat rolls, or kneaded by means of e.g. a kneader, followed by cooling for solidification to obtain a resin composition.

15 However, when particles of at least two groups of particles differing in the average particle size, containing fine particles with an average particle size smaller than 5  $\mu\text{m}$ , are to be added and mixed with the resin as mentioned above under a dry condition, it is extremely difficult to attain uniform mixing, since the dispersion of the particles, particularly the dispersion of the fine particles, in the resin, can not adequately be conducted. Further, even when it is attempted to mix particles of at least two groups of 20 particles containing such fine particles in a dry system, fine particles are likely to coagulate under such a dry condition, and the particles can not be mixed uniformly. Further, a wet system mixing in a solvent such as benzene or toluene was attempted, but it was impossible to obtain a uniform mixing. Even if such a non-uniform mixture is incorporated to the resin, the dispersion and mixing of the particles in the resin will be 25 inadequate, whereby the above-mentioned high packing of the particles or the effect for the flowability of the particles will hardly be attained.

Under these circumstances, the present inventors have succeeded in preparing a resin composition having a filler containing fine particles uniformly dispersed therein, by dispersing and mixing in a polar liquid the groups of inorganic particles, followed by incorporation to the resin. As such a polar liquid, water, an alcohol such as methanol, ethanol or isopropanol, a glycol such as ethylene glycol or propylene glycol, 30 dimethylformamide, or dimethylsulfoxide may, for example be used. The polar liquid is not restricted to such specific examples, and any polar liquid may be used so long as it is capable of dispersing the filler particles under a stabilized condition. Depending upon the particular purpose of the resulting resin composition, the polar solvent may sometimes be restricted. For example, when the resin composition is intended as a sealant for semiconductors, a halogen-containing polar liquid is undesirable.

35 The amount of the polar liquid may be at any level so long as the filler particles can thereby be adequately dispersed. It is used usually in such an amount that the volume % of the filler particles to the sum of the filler particles and the polar liquid is from 5 to 85%, preferably from 10 to 60%.

A usual dispersing or mixing means such as a ball mill or a supersonic dispersing machine may 40 suitably be used for dispersing and mixing the filler particles in the polar liquid.

For the dispersion and mixing of at least two groups of particles, the respective groups of particles may independently be thoroughly dispersed in the polar liquid, and the dispersions of the respective groups of particles in a slurry state may then be mixed, or all of said at least two groups of particles may be added to a polar liquid, followed by dispersing and mixing.

45 The filler particles dispersed and mixed in the polar liquid are usually subjected to the removal of the polar liquid and dried, and then incorporated to the resin as described above.

When the resin can be dissolved in the polar liquid used for dispersing and mixing the filler particles, the resin may be dissolved in the slurry of the polar liquid having the filler particles dispersed and mixed therein, followed by adequate mixing and then by evaporation and removal of the polar liquid to obtain a resin composition.

50 In either case, a care is required to prevent separation of the particles (the separation is likely due to the difference in the sedimentation attributable to the difference in the particle size) or to prevent the separation between the resin and the particles, for example, by stirring, when the polar solvent is removed.

According to the present invention, it is possible to increase the content of the inorganic filler without 55 bringing about a reduction of the flowability. Therefore, according to the present invention, it is possible to obtain a resin composition which has a high inorganic filler content and accordingly a small heat expansion coefficient, excellent heat resistance and yet has high flowability and excellent moldability. Such a resin composition is suitable for various applications including an application as a sealant for semiconductors or as a filler for dental use.

For example, when the resin composition obtained in accordance with the present invention is used as a sealant for semiconductors, it is most common to use an epoxy resin as the resin and silica as the filler, as mentioned above. It is also possible to use, as the resin, an imide resin, an acrylate resin, a liquid crystal polyester, a polyphenylene sulfide, a polyether ether ketone or a polyamide, and as the filler, alumina, 5 titanium silicate, aluminum silicate or aluminum nitride.

As a method for sealing a semiconductor element by using the resin composition having a filler incorporated therein, low pressure transfer molding, injection molding, compression molding and casting, may be mentioned. Among them, the low pressure transfer molding is most common. In the low transfer molding, the resin composition is firstly heated in a pot for plastization and then transferred under a low 10 pressure (at a level of not higher than 70 kg/cm<sup>2</sup>) into a mold, followed by curing and molding. The flowability of the molding material when heated for plastization substantially affects the moldability. The flowability can be evaluated, for example, by the content of particles which can be slurried and by measuring the viscosity by a flow tester, as a simple conventional method.

Now, the present invention will be described in further detail with reference to Examples. However, it 15 should be understood that the present invention is by no means restricted by such specific Examples.

In the following examples, silica was used as the inorganic filler, and a mixture of the resin and additives as identified in the following (1) was used as the resin. The blend proportion (% by volume) of the 20 filler was calculated in accordance with (2). The melt viscosity was measured in accordance with (3).

(1) The resin mixture was prepared by mixing the following resin and additives, in which "parts" 25 means "parts by weight".

Resin:	Cresol novolak epoxy resin	100 parts
Modifier:	Phenol novolak type curing agent	50 parts
Releasing agent:	Epoxy silane coupling agent	2 parts
Pigment:	Carnauba wax	2 parts
	Carbon black	1 part

30 (2) Blend proportion (% by volume) of the filler

The blend proportion was calculated in accordance with the foregoing formula I by applying the density  $\rho$  of the mixture of the resin and additives of the above (1) being 1.1 (g/cm<sup>3</sup>) and the density  $\rho$ -silica being 2.2 (g/cm<sup>3</sup>).

35 (3) Measurement of the melt viscosity

The mixture of the resin and additives of the above (1) and silica as the filler, were kneaded at 80 °C for 15 minutes by heat rolls. The viscosity of the composition thus obtained was measured by a flow tester. The flow tester had an orifice of 2 mm in diameter x 5 mm in length, and the measurement was conducted under a pressure of 10 kg/cm<sup>2</sup> at a temperature of 175 °C.

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EXAMPLE 1

45 90 g of monodisperse spherical silica particles with an average particle size of 0.9  $\mu$ m and a standard deviation ( $\sigma$ ) of 1.05 were added to 215 g of ethanol (volume ratio of silica/ethanol = 13/87) and dispersed for 24 hours by a ball mill. To the resulting slurry, 510 g of pulverized silica particles with an average particle size of 21  $\mu$ m and a standard deviation ( $\sigma$ ) of 1.4 were added to obtain a slurry (volume ratio of silica/ethanol = 50/50). Then, the slurry was heated to 70 °C under stirring and mixing by means of a 50 turbine vane type stirrer, whereby ethanol was removed by evaporation to obtain 600 g of preliminarily dispersed and mixed dry particles. 600 g of the particles were added to 200 g of the resin mixture (1) to obtain the proportions as identified in Table 1, and the mixture was kneaded, whereupon the melt viscosity of the composition thereby obtained was measured.

EXAMPLE 2

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90 g of monodisperse spherical silica particles with an average particle size of 0.9  $\mu$ m and a standard deviation ( $\sigma$ ) of 1.05 and 510 g of pulverized silica particles with an average particle size of 21  $\mu$ m and a standard deviation ( $\sigma$ ) were added to 200 g of the resin mixture (1) without being preliminarily dispersed or

mixed in a polar liquid, and the mixture was kneaded, whereupon the melt viscosity was measured.

5 COMPARATIVE EXAMPLE 1

600 g of pulverized silica particles with an average particle size of 21  $\mu\text{m}$  and a standard deviation ( $\sigma$ ) of 1.4 were added to 200 g of the resin mixture (1) without being preliminarily treated, and the mixture was kneaded, whereupon the melt viscosity was measured.

10 EXAMPLE 3

100 g of monodisperse spherical silica particles with an average particle size of 0.9  $\mu\text{m}$  and a standard deviation ( $\sigma$ ) of 1.05 were added to 295 g of water (volume ratio of silica/water = 13/87) and dispersed for 15 24 hours by a ball mill. To the slurry thereby obtained, 550 g of pulverized silica particles with an average particle size of 21  $\mu\text{m}$  and a standard deviation ( $\sigma$ ) of 1.4 were added to obtain a slurry (volume ratio of silica/water = 50/50). The slurry was heated to 100  $^{\circ}\text{C}$  under stirring and mixing by means of a turbine vane type stirrer, whereby water was removed by evaporation to obtain 650 g of preliminarily dispersed and mixed dry particles. The particles were added as the inorganic filler to 175 g of the resin mixture (1), and 20 the mixture was kneaded, whereupon the melt viscosity of the composition thereby obtained was measured.

COMPARATIVE EXAMPLE 2

25 650 g of pulverized silica particles with an average particle size of 21  $\mu\text{m}$  and a standard deviation ( $\sigma$ ) of 1.4 were added to 175 g of the resin mixture (1) without being preliminarily treated, and the mixture was kneaded, whereupon the melt viscosity of the composition thereby obtained was measured.

30 COMPARATIVE EXAMPLE 3

The same silica particles as used in Example 3 were used in the same ratio (total of 650 g), and they were added to 175 g of the resin mixture (1) without being preliminarily treated. The mixture was kneaded, whereupon the melt viscosity of the composition thereby obtained was measured.

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COMPARATIVE EXAMPLE 4

40 100 g of monodisperse spherical silica particles with an average particle size of 0.9  $\mu\text{m}$  and a standard deviation ( $\sigma$ ) of 1.05 were added to 231 g of cyclohexane (volume ratio of silica/cyclohexane = 13/87), and it was attempted to disperse the mixture by a ball mill, but the obtained mixture was gel-like. To the gel-like mixture, 550 g of pulverized silica particles with an average particle size of 21  $\mu\text{m}$  and a standard deviation ( $\sigma$ ) of 1.4 were added (volume ratio of silica/cyclohexane = 50/50), whereby a uniform slurry was not obtained with the powder scarcely wetted, and no adequate stirring and mixing were possible. The mixture 45 was heated to 70  $^{\circ}\text{C}$ , whereby cyclohexane was removed by evaporation to obtain 650 g of dry particles. The particles were added to 175 g of the resin mixture (1), and the mixture was kneaded, whereupon the melt viscosity was measured.

50 COMPARATIVE EXAMPLE 5

55 100 g of monodisperse spherical silica particles with an average particle size of 0.9  $\mu\text{m}$  and a standard deviation ( $\sigma$ ) of 1.05 were added to 260 g of benzene (volume ratio of silica/benzene = 13/87), and it was attempted to disperse the mixture in a ball mill, but the mixture became gel-like. To the gel-like mixture, 550 g of pulverized silica particles with an average particle size of 21  $\mu\text{m}$  and a standard deviation ( $\sigma$ ) = 1.4 were added (volume ratio of silica/benzene = 50/50), whereby a uniform slurry was not obtained with the powder scarcely wetted, and no adequate stirring and mixing were possible. The mixture was heated to 70  $^{\circ}\text{C}$ , whereby benzene was removed by evaporation to obtain 650 g of dry particles. The particles were

added to 175 g of the resin mixture (1), and the mixture was kneaded, whereupon the melt viscosity was measured.

5 COMPARATIVE EXAMPLE 6

100 g of monodisperse spherical silica particles with an average particle size of 0.9  $\mu\text{m}$  and a standard deviation ( $\sigma$ ) of 1.05 were added to 260 g of toluene (volume ratio of silica/toluene = 13.87), and it was attempted to disperse the mixture in a ball mill, but the mixture became gel-like. To this gel-like mixture, 10 550 g of pulverized silica particles with an average particle size of 21  $\mu\text{m}$  and a standard deviation ( $\sigma$ ) of 1.4 (volume ratio of silica/toluene = 50/50), whereby a uniform slurry was not obtained with the powder scarcely wetted, and no adequate stirring and mixing were possible. The mixture was heated to 100 °C, whereby toluene was removed by evaporation to obtain 650 g of dry particles. The particles were added to 175 g of the resin mixture (1), and the mixture was kneaded, whereupon the melt viscosity was measured.

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EXAMPLE 4

20 80 g of monodisperse spherical silica particles with an average particle size of 0.5  $\mu\text{m}$  and a standard deviation ( $\sigma$ ) of 1.05 and 590 g of spherical silica particles with an average particle size of 22  $\mu\text{m}$  and a standard deviation ( $\sigma$ ) of 1.4 were preliminarily dispersed and mixed in ethanol in the same manner as in Example 1, and then ethanol was distilled off to obtain 670 g of dry particles. The particles were added to 165 g of the resin mixture (1), and the mixture was kneaded. The melt viscosity of the composition thereby obtained was measured.

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EXAMPLE 5

30 130 g of monodisperse spherical silica particles with an average particle size of 0.5  $\mu\text{m}$  and a standard deviation ( $\sigma$ ) of 1.05 and 560 g of spherical silica particles with an average particle size of 22  $\mu\text{m}$  and a standard deviation ( $\sigma$ ) of 1.4 were preliminarily dispersed and mixed in ethanol in the same manner as in Example 4, and then ethanol was distilled off to obtain 690 g of dry particles. The particles were added to 155 g of the resin mixture (1), and the mixture was kneaded. The melt viscosity of the composition thereby obtained was measured.

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COMPARATIVE EXAMPLE 7

40 Spherical silica particles with an average particle size of 22  $\mu\text{m}$  and a standard deviation ( $\sigma$ ) of 1.4 was added to the resin mixture (1) to obtain the proportions as identified in Table 1 without being preliminarily treated with ethanol, and the mixture was kneaded. The melt viscosity of the composition thereby obtained was measured.

45 EXAMPLE 6

50 80 g of monodisperse spherical silica particles with an average particle size of 0.5  $\mu\text{m}$  and a standard deviation ( $\sigma$ ) of 1.05 were added to 274 of methanol (volume ratio of silica/methanol = 10/90) and dispersed for 24 hours in a ball mill. To the slurry thereby obtained, 190 g of spherical silica particles with an average particle size of 7  $\mu\text{m}$  and a standard deviation ( $\sigma$ ) of 1.2 and 490 g of spherical silica particles with an average particle size of 26  $\mu\text{m}$  and a standard deviation ( $\sigma$ ) of 1.2 were added to obtain a slurry (volume ratio of silica/methanol = 50/50). The slurry was then heated to 60 °C under stirring and mixing by means of a turbine vane type stirrer, whereby methanol was removed by evaporation to obtain 760 g of preliminarily dispersed and mixed dry particles. The particles were added to 120 g of the resin mixture (1) to obtain the proportions as identified in Table 1, and the mixture was kneaded, whereupon the melt viscosity was measured.

## EXAMPLE 7

60 g of monodisperse spherical silica particles with an average particle size of 0.9  $\mu\text{m}$  and a standard deviation ( $\sigma$ ) of 1.05 were added to 215 of ethanol (volume ratio of silica/ethanol = 9/91) and dispersed for 5 24 hours in a ball mill. To the slurry thereby obtained, 150 g of spherical silica particles with an average particle size of 26  $\mu\text{m}$  and a standard deviation ( $\sigma$ ) of 1.2 and 390 g of pulverized silica particles with an average particle size of 138  $\mu\text{m}$  and a standard deviation ( $\sigma$ ) of 1.4 were added to obtain a slurry (volume ratio of silica/ethanol = 50/50). Then, the slurry was heated to 70 °C under stirring and mixing by means of 10 a turbine vane type stirrer, whereby ethanol was removed by evaporation to obtain 600 g of preliminarily dispersed and mixed dry particles. The particles were added to 200 g of the resin mixture (1), and the mixture was kneaded, whereupon the melt viscosity was measured.

## COMPARATIVE EXAMPLE 8

15 The spherical silica particles with an average particle size of 26  $\mu\text{m}$  and a standard deviation ( $\sigma$ ) of 1.2 and the pulverized silica particles with an average particle size of 138  $\mu\text{m}$  and a standard deviation ( $\sigma$ ) of 1.4 were added to the resin mixture (1) to obtain the proportions as identified in Table 1 without being 20 preliminarily treated with ethanol, and the mixture was kneaded. The melt viscosity of the composition thereby obtained was measured.

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Table 1

Volume percent (%) of large and small particles in the resin composition							Melt viscosity of the resin composition (Flow tester) (Poise)
Shape of silica (average particle size)	Pulverized (138 µm)	Pulverized (21 µm)	Spherical (26 µm)	Spherical (7 µm)	Spherical (0.9 µm)	Total volume of all particles	Liquid for dispersing silica
Example 1	51			9		60	Ethanol
Example 2	51		9		60		99.6
Comparative Example 1	60				60		110.3
Example 3	55			10		65	Water
Comparative Example 2	65				65		Not measurable*
Comparative Example 3	55				10	65	—
Comparative Example 4	55					65	—
Comparative Example 5	55					65	Cyclohexane
Comparative Example 6	55					65	Benzene
						65	Not measurable*
						10	Toluene
							Not measurable*

Table 1 (continued)

Shape of silica (average particle size)	Volume percent (%) of large and small particles in the resin composition					Melt viscosity of the resin composition (Flow tester) (Poise)		
	Pulver- ized (138 $\mu$ m)	Pulver- ized (21 $\mu$ m)	Spherical (26 $\mu$ m)	Spherical (22 $\mu$ m)	Spherical (7 $\mu$ m)			
					Total volume of all particles			
Example 4	59				8	67	Ethanol	70.7
Example 5	56				13	69	Ethanol	70.0
Comparative Example 7	61				61	-		Not measurable*
Example 6	49	19	8	8	76	Methanol	92.1	
Example 7 Comparative Example 8	39	15	6	6	60	Ethanol	193.4	
	43	17			60	-	Not measurable*	

\* The composition does not pass through the orifice.

It is evident from Table 1 that with respect to the resin containing 60% by volume of the filler, the composition of Comparative Example 1 wherein the filler was composed solely of pulverized particles, had a melt viscosity of 110.3, whereas the composition of Example 2 wherein a part of such particles was substituted by spherical fine particles (average particle size: 0.9  $\mu\text{m}$ ), had a melt viscosity as low as 99.6. Further, the composition of Example 1 wherein the same two groups of particles were used in the same composition and preliminarily treated with ethanol, had a still lower melt viscosity of 79.2, thus indicating improved flowability. Also with respect to the composition containing 65% by volume of the filler, the composition of Example 3 wherein two groups of particles i.e. spherical fine particles and pulverized particles, were used and preliminarily treated with water, had a melt viscosity of 151.8, whereas the composition of Comparative Example 2 wherein only one type of silica particles was used and the compositions of Comparative Example 3 to 6 wherein two groups of silica particles were employed, but no pretreatment was conducted, or treatment was conducted with a non-polar solvent, did not pass through the orifice, and it was impossible to measure the melt viscosity.

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### Claims

1. A resin composition having inorganic filler particles with an average particle size of from 0.05 to 150  $\mu\text{m}$  incorporated in an amount of from 20 to 85% by volume based on the entire resin composition, wherein:
  - (a) said particles comprise at least two groups of particles differing in the average particle size,
  - (b) particles constituting a group of particles with the smallest average particle size, are spherical particles with an average particle size smaller than 5  $\mu\text{m}$ ,
  - (c) a group or groups of particles with an average particle size larger than the particles of (b), are constituted by spherical particles, pulverized particles or a mixture thereof,
  - (d) as between two groups of particles with their average particle sizes being close to each other, the ratio of the minimum particle size within a range defined by the standard deviation of the particle size distribution of the group of particles with a large average particle size, to the maximum particle size within a range defined by the standard deviation of the particle size distribution of the group of particles with a small average particle size, is at least 2, and
  - (e) the proportion of the volume of the group of particles with a large average particle size, to the total volume of the two groups of particles with their average particle sizes being close to each other, is from 20 to 95% by volume.
2. The composition according to Claim 1, wherein the inorganic filler particles are first dispersed in a polar liquid and then incorporated to a resin.
3. The composition according to Claim 2, wherein the polar liquid is at least one member selected from the group consisting of water, an alcohol, dimethylsulfoxide and dimethylformamide.
4. The composition according to Claim 2, wherein the polar liquid is methyl alcohol or ethyl alcohol.
5. The composition according to Claim 1 or 2, wherein the resin is an epoxy resin, and the inorganic filler is silica preliminarily treated with an alcohol.
6. The composition according to any one of Claims 1 to 5, wherein the particles constituting a group of particles with the smallest average particle size, are spherical particles with an average particle size of at most 2.0  $\mu\text{m}$ .
7. The composition according to any one of Claims 1 to 6, wherein as between the two groups of particles with their average particle sizes being close to each other, the ratio of the minimum particle size within a range defined by the standard deviation of the particle size distribution of the group of particles with a large average particle size, to the maximum particle size within a range defined by the standard deviation of the particle size distribution of the group of particles with a small average particle size, is at least 5.
8. The composition according to any one of Claims 1 to 4, 6 and 7, wherein the inorganic filler is at least one member selected from the group consisting of silica, titania, alumina, zirconia, titanium silicate, aluminum silicate and aluminum nitride.
9. The composition according to any one of Claims 1 to 4 and 6 to 8, wherein the resin is at least one member selected from the group consisting of an epoxy resin, an imide resin, an acrylate resin, a liquid crystal polyester resin, a polyphenylene sulfide, a polyether ether ketone, and a polyamide.
10. The composition according to any one of Claims 1 to 9, which is used as a sealant for a semiconductor integrated circuit.
11. A process for preparing a resin composition having a large content of an inorganic filler and yet

having a low viscosity, which comprises dispersing and mixing in a polar liquid an inorganic filler consisting essentially of inorganic particles having an average particle size of from 0.05 to 150  $\mu\text{m}$ , wherein:

- (a) said particles comprise at least two groups of particles differing in the average particle size,
- (b) particles constituting a group of particles with the smallest average particle size, are spherical particles with an average particle size smaller than 5  $\mu\text{m}$ ,
- (c) a group or groups of particles with an average particle size larger than the particles of (b), are constituted by spherical particles, pulverized particles or a mixture thereof,
- (d) as between two groups of particles with their average particle sizes being close to each other, the ratio of the minimum particle size within a range defined by the standard deviation of the particle size distribution of the group of particles with a large average particle size, to the maximum particle size within a range defined by the standard deviation of the particle size distribution of the group of particles with a small average particle size, is at least 2, and
- (e) the proportion of the volume of the group of particles with a large average particle size, to the total volume of the two groups of particles with their average particle sizes being close to each other, is from 20 to 95% by volume, and then, if necessary, after the removal of the liquid, incorporating the filler to a resin in an amount of from 20 to 85% by volume based on the entire resin composition.

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EP 89 11 5836

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 5)
A	CH-A- 656 251 (SPRECHER & SCHUH AG) * Claim 1; page 2, column 2, lines 41-51 *	1,7-9	C 08 K 3/00
A, D	--- CHEMICAL ABSTRACTS, vol. 105, 1986, page 51, abstract no. 44069v, Columbus, Ohio, US; & JP-A-61 34 052 (MATSUSHITA ELECTRIC WORKS, LTD) 18-02-1986	1,7-10	
A	US-A-4 701 479 (SHIOBARA et al.) * Column 3, line 56 - column 4, line 16 *	1,7-10	
	-----		
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C 08 K C 08 L
<p>The present search report has been drawn up for all claims</p>			
Place of search	Date of completion of the search	Examiner	
THE HAGUE	12-12-1989	WILSON A.J.D.	
CATEGORY OF CITED DOCUMENTS			
<p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p>		<p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ..... &amp; : member of the same patent family, corresponding document</p>	



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## EUROPEAN PATENT APPLICATION

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㉑ Compliant thermally conductive compound.

㉒ A compliant thermally conductive, preferably dielectric, compound that enhances the power dissipation capability of high-powered electrical components such as bipolar VLSI semi-conductor chips. The compound has chemically stable thermal conduction and viscosity properties, is not subject to phase separation during use and may be applied in small gaps to maximize thermal conduction. The compound preferably comprises a liquid carrier having thermal filler particles dispersed therein and a coupling agent having a functionality which is reactive with the calcined surface of the thermal filler particles, and a functionality having preferential wetting of the thermal filler particles over self-condensation. Additional additives such as fumed silica and polyisobutylene enhance the phase stability and resistance to thermo-mechanical shear force degradation of the thermally conductive compound encountered during functional usage, e.g., fluctuating power cycles.

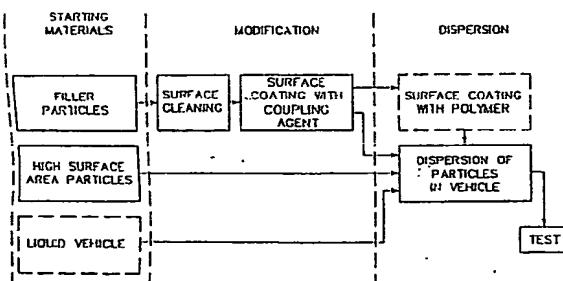


FIG. 3

## Description

## COMPLIANT THERMALLY CONDUCTIVE COMPOUND

The present invention relates to high thermal conductivity, nonbleeding greaselike compounds having a high packing density which are used primarily as a heat transfer means for cooling electronic components such as VLSI chips.

With the high density capabilities and fast switching speeds afforded by VLSI chips, various improved means of dissipating the unprecedented amounts of heat generated by VLSI chips and other solid state components have been pursued. One such means is a thermal compound commonly referred to as thermal grease, which is most commonly used to conduct heat from area arrays of solder-ball attached integrated circuit chips of a packaging module to a heat conducting means or a heat sink as shown in FIG. 1. As VLSI density increases, so does the power of each chip and the associated packaging module when multichip modules are used. The requirements associated with cooling high-powered chips (e.g., state of the art bipolar chips may generate 60 watts per square centimeter area or greater) dictate that the thermal conduction compounds such as thermal grease must have a high thermal conductivity (and preferably being an electrical insulator) while being of low viscosity and compliant so that the thermal compound can be easily applied to the surfaces of the chips to be cooled and can conform ultimately with the microscopically rough surface of the chips, which are often bowed or tilted to minimize air gaps which are detrimental to the cooling process. Low viscosity is also required because the chips and solder bonds that usually attach the chips to a substrate are fragile and the force applied by the thermal grease to the chip must be minimal in magnitude while maximum in contact to minimize interface thermal resistance so that a good thermal path is formed. It is a further requirement that the thermal grease compound be able to withstand power cycling at high chip powers with the attendant mechanical stresses arising from the differences in coefficients of thermal expansion of the various material systems over the life of a module without the compound degrading significantly in thermal conductivity or mechanically, such as experiencing phase separation between the liquid and solid components of the compound.

There are numerous thermal grease compounds available in the art. Heretofore, however, none have satisfied the combined requirements of high thermal conductivity, high electrical resistivity, low viscosity, compliance, and resistance to phase separation or degradation in property stability (thermal conductivity, viscosity, etc.) of the present invention. For example, U.S.-A-3.405.966 teaches the use of particles such as boron nitride or silicon dioxide in a dielectric fluid such as mineral oil for the purposes of conducting heat from electrical devices and equipment. The use of the U.S.-A-3.405.966 thermal grease in state of the art VLSI systems wherein chip powers exceed 30-60 watts per square centimeter has been found not to be adequate because the heat conductive particles separate from the dielectric liquid carrier when the chips experience fluctuating power cycling during their operation, (chips experience temperature differences of greater than 50 degrees centigrade between the inactive and fully active states). This phase separation leads to a decrease in thermal conductivity wherein the thermal compound would eventually not be adequate to dissipate the required amount of heat from the semiconductor chips.

U.S.-A-3.882.033 to Wright teaches that organopolysiloxane grease compositions having good dielectric and heat transfer properties can be obtained by utilizing certain proportions of poly-siloxane fluid, a dielectric desiccant selected from anhydrous calcium sulfate and synthetic zeolites, and a grease thickening and thermal conducting agent. Materials such as anhydrous calcium sulfate and synthetic zeolite have lower intrinsic thermal conductivities compared with the particles described in the present invention. Also, no means or process is shown for achieving high particle packing density to further increase thermal conductivity or to inhibit separation of the particles from the liquid carrier in such pastes in contact with chips operating at high and fluctuating power cycling.

A flexible heat conducting sheet having thermally conducting boron nitride particles dispersed within is described in the IBM TDB dated April 1983, pp. 5740-5743 by Lacombe et al. Lacombe et al. used polyisobutylene (PIB) as the organic carrier which has a very high loading density of boron nitride particles in the carrier. This is not suited for the present application wherein low viscosity and compliance is required in a mobile dielectric medium so that the thermal compound can intimately conform to the semiconductor devices to be cooled.

The thermal compound must also be applied as a thin layer so that the thermal path is as small as possible. The small gap results in excessive mechanical shear stress on the thermal compound that, when combined with thermal stress from high temperatures and power cycling, causes phase separation during power cycling of thermal compounds heretofore known. Low viscosity is also required to accommodate chip tilt and any chip surface irregularities while the thermal grease compound must exhibit rapid stress relaxation to limit the amount of force transmitted to the chips.

IBM TDB dated March 1983, pp. 5322 by Mondou et al describes the use of boron nitride particles in a poly(alphaolefin) carrier with wetting agents incorporated therein. The particles in Mondou et al are not at a higher surface energy than the carrier, thus wetting of the particle surfaces by the organic carrier is not spontaneous. This reference does not suggest the unique characteristics required and taught by the present invention, which allow for high thermal conductivity, high electrical resistivity, low viscosity, and chemical stability (does not oxidize or cause corrosion, keeps thermal conductivity and viscosity relatively constant) while eliminating phase separation during power cycling. A similar thermal grease is described by Mondou et al

in the IBM TDB dated March 1983, pages 5320-21 wherein it is indicated that the thermal conductivity is greater than 1,25 Watts per meterdegree C (W/m°C). This compound also will not provide high thermal conductivity while also providing low viscosity and eliminating phase separation during power cycling of the high powered chips required in state of the art VLSI and VLSI applications.

IBM TDB to Aakalu et al. dated Dec. 1981, pp. 3530 employs a thermally conductive powder dispersed in a mobile hydrocarbon fluid, resulting in a dielectric medium. Aakalu et al. teach the use of hydrated silica to enhance the resistance of the thermal grease to phase separation. The thermal conductivities achieved by this thermal grease are in the range of 1 Watt per meterdegree C with 71,4 weight percent boron nitride loading. This relatively high loading results in a paste having a viscosity that causes the paste to be not mobile enough to be placed into thin gaps without threatening either cracking large area chips and/or their associated solder bonds when applied thereto. In addition to the relative high viscosity of the Aakalu et al. TDB, it has been found by the inventors that phase separation occurs if this type of compound is powered at high fluctuating power cycling levels, causing a mechanical shearing of the applied thin film of the thermal grease compound. i.e. in the range of greater than 30 to 60 W/cm<sup>2</sup>.

U.S.-A-4.265.775 to Aakalu et al. describes a thermal filler powder of laminar or dendritic shapes in a silicone liquid carrier which incorporates silica fibers to help prevent bleeding of the particles from the liquid carrier due to its high surface area. Even though this disclosure inhibits bleeding for certain applications, it has been found that at repeated power cycling and chip temperatures over 80°C that bleeding is not prevented by the addition of mere silica alone. Moreover, the wetting agents and liquid carrier described in the U.S.-A-4.265.775 thermal compound are not suitable for the present application because they cannot be removed completely by solvents; and thus causes metallurgical non-wetting problems during rework of solder joints, and contamination of other surfaces in multichip packages and the tooling (i.e. furnaces, etc.) used for assembling such packages.

In view of the above there exists a need in the art for stable thermal conducting compounds having a high thermal conductivity and high electrical resistivity, while also having a relatively low viscosity so that compound exists as a mobile medium which can easily be applied and conformed to, and wet the surface of the chips to be cooled while not exerting forces to crack the chips or solder bonds which attach the chips to substrates. It is also required that there be no phase separation between the liquid carrier and thermally conductive particles, or degradation in viscosity or thermal conductivity during power cycling of high powered VLSI and VLSI chips and that the thermal compounds are capable of being applied in thin layers so that the total thermal resistance path through the thermal compound is as low as possible. The thermal compound must also be capable of withstanding reciprocating mechanical shear stress during power cycling. Such thermal mechanical stressing occurs when the thermal compound is in the small gap between a chip and an internal thermal enhancement such as a spring loaded piston as shown in FIG. 1B, or between the chip and a cap as shown in FIG. 1A. There is also a need for the compound to be readily cleanable from chips and metal surfaces to facilitate rework of chips.

A primary object of the present invention is to provide a phasestable, thermally conductive compound, having a relatively constant thermal conductivity and viscosity, for transferring heat form electronic compounds, such as integrated circuit chips, wherein no phase separation occurs between the thermally conductive particles therein and the dielectric liquid carrier when the compound is exposed to high heat loads (i.e. 30-60 W/cm<sup>2</sup> or greater) with temperature variations during power cycling.

A further object of the present invention is to provide such compounds having a relatively high packing density of thermally conductive particles and high thermal conductivity, while also having a low viscosity so that the compound is a mobile medium which can be applied easily and conform to the surface of integrated circuit chips, without cracking the chips or solder bonds between chips and substrate.

It is a further object that the thermally conductive compound be capable of wetting surfaces when being applied in thin layers in gaps to provide as low a stable thermal resistance as possible, and withstand the shear forces without phase separation that result when such a compound is applied to a thin gap between an integrated circuit chip and internal thermal enhancement device which are subjected to fluctuating power densities causing thermomechanical stressing of the thermal compounds.

Still further objects are that the thermally conductive compound be electrically insulating so that the electrical function of the integrated circuit chip will not be interfered with and that the compound be cleanable in common to facilitate rework.

A further object is that the particles be evenly dispersed in, and wet by, the liquid carrier and do not flocculate during use.

A further object is that the thermally conductive compound be solvent cleanable from surfaces of materials used in the semiconductor packaging industry.

These objects as well as other advantages are accomplished by the present invention which provides a phase-stable, thermally conductive compound having at least a dielectric, (preferably a chemically saturated oily hydrocarbon liquid carrier;) thermal filler particles of higher surface energy than the liquid vehicle, and a high thermal conductivity, such as calcined boron nitride or aluminum spheres having an anodized aluminum coating evenly dispersed through the carrier; and a coupling agent from the class of organometallics, (e.g., from the group of organosilanes, organo-titanates, organoaluminates, or organozirconates), having a functionality which is reactive with the surface of the particles, and a functionality having a preferential wetting of the particles over selfcondensation. The preferred thermal compound also contains high surface area

fumed silica to resist the propensity of the oily liquid to separate from the compound at extremely high operating temperatures or during excessive power cycling over extended periods of time; as well as a chemically stable polymer (e.g., polyisobutylene) which further prevents phase separation when it is applied in a way to foster preferential adsorption on the particles and thereby stabilize the dispersion, (i.e. resist flocculation of particles). The compound is of low viscosity and has low surface energy to conform to and wet the surface of the chips of varying roughness, tilts, and heights, (e.g. preferably viscosity between approximately 2 million centipoise and approximately 20 million centipoise), while having a high particle packing density for maximum thermal conductivity and maintaining consistent particle dispersion through-out, preventing phase separation because the absorbed polymer serves to prevent intrinsic aggregation of particles through entropic repulsion, and concomitantly has a chemical structure similar to that of the hydrocarbon oil to cause an affinity between them. To best accomplish this, it is most preferred that the thermal filler particles be cubic or spherical in shape for optimum loading and minimum viscosity. The phase stable compound is not corrosive to materials usually used in high performance VLSI packages such as solder, copper, molybdenum, chromium, ceramic, etc. and is easily and completely removable from such materials by simple organic solvents so that packages may be metallurgically reworked without experiencing nonwettable metallurgical surfaces due to residual low surface energy organic residues. A process sequence that must be followed to successfully make the stable thermally conductive compound is also disclosed.

FIGS. 1A and 1B show typical semiconductor packages in which the thermal compound of the present invention may be used.

FIG. 2 is a graph of the resistance to phase separation and power cycle lifetimes as a function of viscosity of various thermal compounds within the scope of the present invention.

FIG. 3 is a flow chart depicting the preferred process for forming the phasestable and thermally stable conductive compound of the present invention.

The present invention provides a novel thermally conductive greaselike compound which has heretofore not existed in the art, and which has advantages and performance that was not heretofore possible in the art. The thermally conductive compound is of low viscosity, typically in the range of 2 million to 20 million centipoise at 100°C, which makes it a low viscosity greaselike or pastelike substance which is compliant enough to follow the contour of and chemically wet semiconductor chips or the cooling surfaces in contact with semiconductor chips mounted on a packaging substrate regardless of variations in chip tilt or chip height which are commonplace in state of the art multichip modules, especially those using area arrays of solder balls for chip connections as described in U.S.-A-3.495.133, entitled "Circuit Structure Including Semiconductive Chip Devices Joined to A Substrate by Solder Contacts". Specific components of working examples made in accordance with the thermally conductive greaselike compound of the present invention are listed in TABLE I, wherein specific thermal filler particles are dispersed throughout a chemically matched liquid carrier, and selected classes of additives which enhance dispersion and stability are incorporated. The liquid carrier is typically an oily, solvent cleanable dielectric fluid, preferably a hydrocarbon liquid carrier, which is nonpolar and chemically saturated so that it does not absorb moisture and thereby cause corrosion of thin metal films in the module. The liquid carrier retains the thermal filler particles which are evenly dispersed throughout the liquid carrier and remain dispersed through the life of the compound due to the novel formulation disclosed herein.

For the resulting compound to be mobile and compliant, the liquid carrier should typically have a viscosity of approximately 30 centipoise to about 500 centipoise at 100°C. Preferred are nonpolar, low surface energy organic fluids having a viscosity of 40 to 150 centipoise at 100°C. Dielectric fluids such as mineral oil and synthetic mineral oil (e.g., synthetic poly(alphaolefin)), are acceptable, and preferred are fluids which can be represented by the the following chemical formula:

45 R R

| |

50 - (C-C) - x

| |

R R

55 where X is 6 - 50

and R is H, or alkyl substituents.

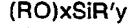
The most preferred liquid carrier is chemically saturated poly(alpha-olefin) having a viscosity of approximately 80-120 centipoise at 100°C. The polarity of the carrier should preferably match the polarity of certain additives which will be described hereinafter. The polarities should match because this promotes mutual affinity so that phase separation is minimized. It is most preferred that the polarity of the carrier be nonpolar so that the affinity for moisture will be low and corrosion will not occur.

The thermal filler particles exhibit a relatively high thermal conductivity, (for example, boron nitride, vanadium boride, and aluminum spheres coated with an anodized aluminum coating, and combinations thereof). The preferred shape is uniform spheres or cubes so that packing density is maximized while providing a low viscosity of the dispersion of particles in an oily nonpolar vehicle that enables uniform

dispersion of particles and inhibits flocculation. Even though uniform spheres or cubes are most preferred, the present invention meets the above objects with thermal particles of alternative shapes such as platelets. The higher packing density aids in the reduction of phase separation, and provides a conduction system that facilitates high thermal conductivity. Dispersion of the particles, reduction of phase separation and lower viscosity are further facilitated by the addition of a coupling agent, which will be described hereinafter.

The particles are preferably electrical insulators so that they can readily be utilized in multichip modules used in VLSI computer systems which in many instances require electrical isolation between chips on the multichip modules. It is imperative that the thermal filler particles be higher in surface energy than the liquid carrier so that the liquid carrier adequately wets the particles. This is accomplished by treating the particles so that they are free of contaminants, particularly adsorbed organic compounds. It has been found that this is most efficiently done if the thermal filler particles are calcined. Alternative methods such as RF plasma ashing may be used to treat the surface of the particles. In the working examples that follow, all particles are calcined unless otherwise noted. The preferred volume percentage of thermal filler particles in the liquid carrier is between approximately 25% and 65% and foreseeably could be higher depending on the required compliance of the thermal compound. Even though it is commonly practiced by those skilled in the art to increase the volume concentration of the thermal filler particles to increase the thermal conductivity of thermal compounds such as thermal grease, it has been found in the present invention that very high packing densities make the resulting thermal compound noncompliant, and sensitive to mechanical fracture during power cycling, and that such high packing densities do not necessarily result in the highest thermal conductivities. It is preferred that the aforementioned treated thermal filler particles be oleophilic after treatment so that the particles will be wetted by the low surface energy, solvent cleanable liquid carrier to facilitate dispersion and rework. The novel combination of liquid carrier and thermal filler particles described above in addition to the other components of the present invention to be described hereinafter and their relative proportions provide a high thermal conductivity of greater than 1,3 W/m°C while being compliant and meeting the phase separation criteria as well as other objectives of the present invention.

A critical component of the present invention is a coupling agent. Preferably, the agent is applied on the particle surfaces, and functions to decrease the phase separation between the liquid carrier and thermal filler particles and foster lower viscosities by dispersing the thermal filler particles and preventing their flocculation at high power densities, which are encountered in state of the art VLSI modules. The coupling agent has at least one functionality which is reactive with the preferably calcined surface of the thermally conductive filler particles and at least one functionality which is of similar polarity as the liquid carrier. The coupling agent has a preferential wetting of the particles over self-condensation. It is preferred that there be some self-condensation as well to provide a veneer around the particles to thereby lessen the tendency of the particles to flocculate. The coupling agents meeting these functional criteria are typically selected from the group consisting of organosilanes, organotitanates, organoaluminates, or organozirconates. The preferred operable organosilanes are represented by the formula:



wherein  $x + y = 4$ ;  $x, y = 0$  (preferably  $x = 3, y = 1$ )

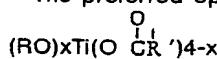
$R = CnH2n+1$ ,

$R' = CnH2n+1$

$n > 10$

The functionality which is reactive with the thermally conductive filler particles is (RO) and the functionality which is of similar polarity as the liquid carrier is (R').

The preferred operable organotitanates are represented by the formula:

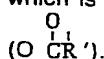


wherein  $R = CnH2n+1$

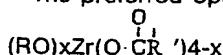
$R' = CnH2n+1$ ,

$n > 7$

The functionality which is reactive with the thermally conductive filler particles is (RO) and the functionality which is of similar polarity as the liquid carrier is:



The preferred operable organozirconates are represented by the formula:

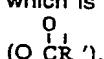


wherein  $R = CnH2n+1$

$R' = CnH2n+1$ ,

$n > 7$

The functionality which is reactive with the thermally conductive filler particles is (RO) and the functionality which is of similar polarity as the liquid carrier is:



The preferred operable organoaluminates are represented by the formula:

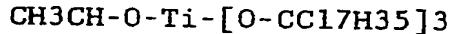


wherein

$n + m = 3, n = /0$

$R, R', R'' = CnH2n + 1$

5 In the most preferred embodiments wherein the liquid carrier is a chemically saturated solvent soluble poly(alpha-olefin), and any calcined boron nitride particles or aluminum spheres coated with an anodized layer are dispersed throughout, the preferred coupling agent is isopropyl triisostearoyl titanate.



15 The range of percentages of the coupling agent in the stable thermal compound of the present invention is between 0.5 and 10 weight percent. Precise compositions are specifically taught in the working examples which follow hereinafter. Preferably, the polarity of one part of the coupling agent must be nonpolar to match the chemical nature of the poly(alpha-olefin) liquid carrier, so that the properties (i.e. thermal conductivity, viscosity, etc.) of the compound remain stable at high VLSI operating temperatures and during power cycling, and the compound does not experience excess phase separation.

20 In addition to providing a compound having excellent thermal conductivity while being compliant to conform to, and wet the higher surface energy surfaces of cleaned semiconductor chips, and not exhibiting phase separation between the thermal filler particles and liquid carrier while remaining stable during power cycling; the basic components are combined to satisfy other requirements of state of the art VLSI multichip modules. The basic components can be combined depending on the specific system requirements. The stability of the 25 thermally conductive compound in preferred form is further enhanced by the addition of chemically inert particles of high surface area to resist phase separation by absorbing excess liquid carrier in those situations where chip power cycling leads to thermal/mechanical stressing of the compound and a propensity for the compound to bleed. It has been found that in the present phase and property stable thermal compound consisting of an organic liquid carrier, thermal filler particles evenly dispersed therein, and a coupling agent as described above, that fumed silica particles of approximately 100-300 m<sup>2</sup>/gram in surface area increase the capacity of the compound to avoid irreversible bleeding. It is preferred that the fumed silica be treated to provide a polar, hydrophobic surface, for example, by silicating surface hydroxyl groups. The hydrophobicity improves the affinity of the fumed silica for the liquid carrier of the present invention. The hydrophobic fumed silica has little or no tendency towards self-agglomeration, so that it provides a minimal viscosity increase 35 when added to the thermal compound of the present invention. The coupling agent also enhances particle dispersion so that lower viscosity is attainable while thermal conductivity is maximized.

30 In addition to the thermal compound having a high thermal conductivity, it is known to those skilled in the art that the thermal compound or thermal grease must be applied in as thin a layer as possible to achieve maximum thermal performance. When the low viscosity thermal compound of the present invention is applied to a small gap (e.g., 0.05 mm or less) between a chip and internal thermal enhancement (see FIG. 1B), the resultant shear forces that are applied to the grease-like thermal compound are relatively high and are a further cause of phase separation and structural damage to the thermal compound, especially during power cycling. This results in a reduced capacity to dissipate heat. It has been found that in the present stable thermal compound that the addition of a polymer that readily dissolves in the chosen liquid carrier enhances the shear 40 stability of the compound. The role of the polymer helps the compound to resist flocculation of particles and the attendant phase separation. To facilitate rework of a multichip module, the polarity of the polymer should preferably match that of the oily carrier liquid. This allows the resultant compound to be easily removed by organic solvents from surfaces that the compound may typically be exposed to. In VLSI semiconductor modules, such surfaces are semiconductor materials, solders, insulators such as ceramic, and metals such as 45 gold, copper, molybdenum, chromium, and titanium. The preferred polymer is a nonpolar elastomer which matches the polarity of the preferred poly-(alpha olefin) liquid carrier, namely polyisobutylene. The resultant thermal compound is also non-corrosive toward the packaging materials due to its hydrophobicity. It is also 50 advantageous to incorporate an antioxidant so that any inadvertitous exposure of the compound to oxygen or other oxidizing agents will not cause a chemical change causing phase separation.

55 The above described components can be combined in various proportions as taught by the working examples which follow hereinafter. The general process requirements for forming the various stable thermal compounds embodied by the present invention in the working examples are as shown in the flow chart of FIG 3 and are described as follows.

60 Generally, the thermally conductive particles are treated before they are dispersed throughout the liquid carrier so that their surfaces are activated. The particle surfaces are first activated by heat treating, preferably calcining in air, in order to remove low surface energy organic contaminants adsorbed from the ambient (e.g., during storage), and so that they are capable of interacting with the coupling agent. After activation, the particles are coated with a coupling agent, (i.e., typically an organosilane, organotitanate, organozirconate, or organoaluminate, as described above), which renders it more readily dispersible in the liquid carrier in which 65 the particles are to eventually be dispersed by breaking up agglomerates of particles and thereby lowering

viscosity of the dispersion. After the particles are thus coated, they are preferably coated with a polymer (e.g., polyisobutylene) by solution/solvent removal techniques, after which, they are dispersed into the liquid carrier until a homogeneous compound is formed. The polyisobutylene is not essential for all operating conditions. In a system having boron nitride particles of approximately 0,01 to 30 microns in diameter, and a synthetic mineral oil such as a high viscosity poly-(alpha-olefin) as the liquid carrier, the dispersion is preferably accomplished by shearing with a conventional three roll mill, so that the particles are evenly dispersed throughout the compound. It has been found that the optimum amount of coupling agent to be coated onto the particles is determined by coating the particle surface with the coupling agent until no further lowering of the viscosity of the resulting compound occurs. The coupling agent amount that provides the lowest viscosity is adequate for providing even particle dispersion and preventing phase separation while providing a mobile medium which can conform to the surface contour of the chips without causing undue forces on the chips which could fracture the chips or the solder bonds which connect them to the semiconductor package. The addition of polyisobutylene for shear stability, or fumed silica may be accomplished by techniques noted above and indicated in the process flow diagram of FIG. 3.

The resultant compound must be of low enough viscosity to be mobile during module assembly to follow the surface contour of chips, but must be viscous enough so as to be stable mechanically when applied in small gaps to form the heat conductive path, especially when exposed to power fluctuations. In state of the art semiconductor modules, these gaps are as low as 0,05mm or less to minimize the length of the thermal path. This small gap causes high shear forces to be applied to the thermal compound, which adds to the stability problem. To satisfy these criteria, as well as accomplishing all of the other advantages provided by the thermally conductive compound of the present invention, it is preferred that the compound comprise from approximately 25% by volume to approximately 65% by volume of thermally conductive filler particles, from approximately 0.5% by weight to approximately 10% by weight of coupling agent, and the balance being the liquid carrier. If desired or required, approximately 1% to approximately 6% by weight of fumed silica particles and/or approximately 2% to approximately 6% by weight polyisobutylene are also added. The thermally conductive compound of the present invention has been generally described above. The following are preferred examples of practicing the present invention. In the examples; the boron nitride particles have an average particle size, (i.e., equivalent spherical diameter), of 1 micron, while the aluminum spheres have an average size of 5-15 microns, and the vanadium boride particles have an average particle size of 1-8 microns. The examples using boron nitride filler particles have been tested for stability and phase separation by accelerated testing methods, (i.e. centrifuge process, actual power cycling or both). In each example, the thermal compound was applied in a gap of approximately 0,05mm, in a module as depicted in FIG. 2, and then power cycled. The preferred thickness range that the thermal compound should be applied in is from 1 to 10 mils to facilitate high thermal conductivity. The centrifuge conditions were at 55°C for 24 hours at an acceleration of approximately 1800 times the gravitational force. It has been found that thermal compounds which exhibit relatively good stability during centrifuge testing are also stable during power cycling. The power cycling conditions were such that the grease-like thermal compound experienced temperature variations of approximately 60°C twice an hour in an approximately 0,05mm gap between a chip and module hardware. The available power cycling and centrifuge data is included in the working examples. In each working example, the thermally conductive compound was readily removed by common solvents such as hexane, toluene, and other solvents known to those skilled in the art, and was not corrosive to any module components.

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SUMMARY OF WORKING EXAMPLES

EXAMPLE	BASIC MATERIALS	VOLUME % SOLID	VISCOOSITY (Million cps)	THERMAL CONDUCTIVITY (W/M°C)	EXTRACTABLE OIL (%)	# OF POWER CYCLES TO PHASE SEPARATION
<b>Prior Art</b> (e.g. Nondou et al IBM TDB, 3/83, p. 5322)						
#1	Boron Nitride Mineral Oil Organotitanate	33	12	1.1	8	<150
#2	Boron Nitride Polyalphaolefin Oil Organotitanate Polymer	33	11	1.4	7	>3000
#3	Boron Nitride Polyalphaolefin Oil Organotitanate Polymer Silica	32	9	1.3	7.5	>1500

SUMMARY OF WORKING EXAMPLES

EXAMPLE	BASIC MATERIALS	VOLUME % SOLID	VISCOOSITY (Million cps)	THERMAL CONDUCTIVITY (W/M°C)	EXTRACTABLE OIL (%)	# OF POWER CYCLES TO PHASE SEPARATION
#4	Boron Nitride Polyalphaolefin Oil Organotitanate	32	8	1.0	4.5	-
#5	Boron Nitride Polyalphaolefin Oil Organosilane	32	10	1.4	6.9	-
#6	Oxide Coated Aluminum Spheres Polyalphaolefin Oil Organotitanate	59	15	3.2	-	-
#7	Vanadium Boride Polyalphaolefin Oil Organotitanate	50	5	1.8	-	-

## EXAMPLE 1:

Boron nitride thermal filler particles of approximately 0,01 to 44 microns in equivalent spherical diameter each were calcined and then coated with 0,44 grams of an organotitanate coupling agent isopropyl triisostearoyl titanate, i.e. C<sub>3</sub>H<sub>7</sub>OTi(OOCC17H35)3. 28 grams of the coated boron nitride particles and 22 grams of mineral oil were mixed by roll milling. The resultant roll-milled thermal compound has a viscosity of approximately 11 million centipoise. The thermal conductivity is 1,4W per meter°C. The grease-like thermal compound was stable for over 3000 power cycles without phase separation, and 7 percent by weight of oil was extracted from the compound during accelerated centrifuge testing.

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## EXAMPLE 2:

Boron nitride thermal filler particles of approximately 0,01 to 44 microns in equivalent spherical diameter each were calcined and then coated with 1,1 grams of an organotitanate coupling agent isopropyl triisostearoyl titanate, i.e. C<sub>3</sub>H<sub>7</sub>OTi(OOCC17H35)3. 55 grams of the coated boron nitride particles and 0,1 gram of an antioxidant (a sterically hindered phenol such as tetrakis (methylene(3,5-ditertbutyl-4-hydroxyhydro-cinnamate) methane) were mixed with 45 grams of a synthetic poly(alphaolefin) oil having a viscosity of 40 centipoise by roll-milling. 1,1 gram of polyisobutylene was added to the mixture. The resultant roll-milled thermal compound has a viscosity of approximately 9 million centipoise and has a thermal conductivity of approximately 1,3 W per meter°C. The compound was stable for over 1500 power cycles without phase separation, and 7,5 percent by weight of oil was extracted from the compound during accelerated centrifuge testing.

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## EXAMPLE 3:

Boron nitride thermal filler particles of approximately 0,01 to 44 microns in equivalent spherical diameter each were calcined and then coated with 1,1 grams of an organotitanate coupling agent isopropyl triisostearoyl titanate, i.e. C<sub>3</sub>H<sub>7</sub>OTi(OOCC17H35)3. 54,9 grams of the coated boron nitride particles and 0,21 grams of a sterically hindered phenol antioxidant; (i.e. tetrakis (methylene(3,5-ditertbutyl-4-hydroxyhydro-cinnamate) methane) as per example 4) were mixed with 41 grams of a synthetic poly(alpha-olefin) oil having a viscosity of 100 centistokes by roll milling. 1,1 grams of poly-isobutylene and 1,6 grams of a hydro-phobic (average surface area of 100 m<sup>2</sup>/gm) fumed silica were added to the mixture. The resultant roll-milled thermal compound has a viscosity of approximately 13 million centipoise and has a thermal conductivity of approximately 1,4 W per meter°C. The compound survived power cycling for over 4000 cycles without phase separation, and had 1,50% by weight of oil extracted during accelerated centrifuge testing.

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## EXAMPLE 4:

Boron nitride thermal filler particles of approximately 0,01 to 44 microns in equivalent spherical diameter each were calcined and then coated with 0,56 grams of an organotitanate coupling agent, n-propyl tri-n-decanoyl titanate, n-C<sub>3</sub>H<sub>7</sub>Ti(OOCC9H19)3. These coated particles were mixed into a poly(alpha-olefin) liquid carrier. Approximately 28 grams of the boron nitride particles and approximately 22 grams of the liquid carrier were mixed by roll milling. The resultant roll milled thermal compound has a viscosity of approximately 8 million centipoise. The thermal conductivity is 1,0 W per meter°C. The compound had 4,6% by weight oil extracted during accelerated centrifuge testing.

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EXAMPLE 5:

Boron nitride thermal filler particles of approximately 0,01 to 44 microns diameter each were calcined and then coated with 0,44 grams of an organosilane coupling agent octa-decyltrioxysilane (C<sub>2</sub>H<sub>5</sub>O)3SiC<sub>18</sub>H<sub>37</sub>. Approximately 28 grams of the coated boron nitride and approximately 22 grams of poly(alpha-olefin) oil were mixed by roll milling. The resultant compound has a viscosity of approximately 10 million centipoise. The thermal conductivity is 1,4 W per meter°C. The compound had 6,9% by weight oil extracted during accelerated centrifuge testing.

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## EXAMPLE 6:

90 grams of spherical aluminum filler particles coated with a thin oxide coating were combined with 8 grams of boron nitride filler particles. The particles were coated with approximately 1,6 grams of the organotitanate coupling agent of example 1. These particles were roll milled with 19,6 grams of synthetic poly-(alpha-olefin) oil of 40 centipoise viscosity. The resultant compound has a viscosity of approximately 15 million centipoise. The thermal conductivity is approximately twice as high as that of example 1, i.e., approximately 3,2 W per meter°C.

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## EXAMPLE 7:

83,7 grams of vanadium boride particles and 0,1 gram of antioxidant (a sterically hindered phenol, in this case, tetrakis (methylene (3,5-ditert-butyl- 4-hydroxyhydro-cinnamate)methane) were mixed and the particles were coated with approximately 0,8 grams of the organotitanate coupling agent of example 1. The coated particles were roll milled with 15,4 grams of poly(alpha-olefin) oil having a viscosity of 100 centipoise. The resultant compound has a viscosity of approximately 5 million centipoise. The thermal conductivity is approximately 1,8 W per meter°C.

FIG. 2 graphically depicts the stability of working examples 1-5 of the present invention as a function of viscosity. Where available, both centrifuge and power cycling data are shown. It is evident that the working examples of the present invention provide stability of the thermal compound with corresponding low viscosity. Working examples 6 and 7, (thermal filler particles of oxide coated aluminum spheres and vanadium boride, respectively), provide even higher thermal conductivities at similar viscosity ranges as working examples 1-5. The compounds having oxide coated aluminum spheres and vanadium boride thermal filler particles have relatively low viscosities that are useful in the applications envisioned by the present invention. The low viscosity is primarily because of the enhanced dispersion and resistance to thermal filler particle flocculation and reflocculation provided by the coupling agents. An additional advantage of the low viscosity is that a greater number of thermal filler particles may be added to the compound if even greater thermal conductivity is required.

While the invention has been described in detail, and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made without departing from the spirit and scope of the present invention.

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## Claims

1. A thermally conductive compound characterized in that it comprises:  
a liquid carrier;  
thermally conductive filler particles dispersed throughout said liquid carrier;  
said particles being higher in surface energy than said liquid carrier so that said liquid carrier wets said particles; and  
a coupling agent having at least one functionality which is reactive with the surface of said thermally conductive filler particles and at least one functionality which is of similar polarity of said liquid carrier.
2. The compound of Claim 1 wherein said coupling agent has a preferential wetting of said particles over self-condensation and is selected from the group consisting of organosilanes, organotitanates, organoaluminates, and organozirconates.
3. The thermally conductive compound of Claim 1 or 2 further comprising high surface area inert particulate additives that adsorb excess carrier liquid.
4. The thermally conductive compound of Claim 3 wherein said high surface area inert additive comprises fumed silica.
5. The thermally conductive compound according to any one of the preceding claims wherein said functionality which is reactive with the surface of said thermally conductive filler particles is (RO), wherein R = C<sub>n</sub>H<sub>2n+1</sub>.
6. The thermally conductive compound according to any one of the preceding claims wherein said functionality which is of similar polarity of said liquid carrier is R', wherein R' = C<sub>n</sub>H<sub>2n+1</sub>.
7. The thermally conductive compound according to any one of the claims 1 to 5 wherein said functionality which is of similar polarity of said liquid carrier is:  
O  
(O CR'), wherein R' = C<sub>n</sub>H<sub>2n+1</sub>.
8. The thermally conductive compound of Claim 4 wherein the surface area of said fumed silica is hydrophobic and corresponds to 100-300 m<sup>2</sup>/gram.
9. The thermally conductive compound according to any one of the preceding claims having high particle packing density and being capable of maintaining particle dispersion in a low viscosity compound.
10. The thermally conductive compound according to any one of the preceding claims further comprising a nonpolar polymer that readily dissolves in said liquid carrier.
11. The thermally conductive compound of Claim 10 wherein said nonpolar polymer is an elastomer.
12. The thermally conductive compound of Claim 11 wherein said elastomer is polyisobutylene the polarity of which matches the polarity of said liquid carrier.
13. The thermally conductive compound according to any one of the preceding claims wherein said liquid carrier is chemically saturated, nonpolar and a dielectric.
14. The thermally conductive compound according to any one of the preceding claims wherein the viscosity of said liquid carrier is between approximately 30 and 500 centipoise at 100°C and the viscosity of said compound is between approximately 2 and 20 million centipoise at 100°C.
15. The thermally conductive compound according to any one of the preceding claims wherein said liquid carrier is poly(alpha-olefin).
16. The thermally conductive compound according to any one of the preceding claims further comprising an antioxidant.
17. The thermally conductive compound according to any one of the preceding claims wherein said thermally conductive filler particles are platelet, spherical, or cubic in shape.
18. The thermally conductive compound according to any one of the preceding claims wherein said particles are selected from the group consisting of boron nitride, aluminum spheres coated with Al<sub>2</sub>O<sub>3</sub>, and vanadium boride.
19. The thermally conductive compound according to any one of the preceding claims wherein said

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thermally conductive filler particles are electrical insulators and wherein the volume percent of thermally conductive filler particles is between 25 and 65 percent.

5 20. The thermally conductive compound according to any one of the preceding claims wherein said liquid carrier is easily removable by organic solvents from solders, molybdenum, gold, copper, chromium, or titanium and is noncorrosive to solders, molybdenum, ceramic, gold, copper, chromium, or titanium.

10 21. The thermally conductive compound according to any one of the preceding claims wherein the surfaces of said thermally conductive filler particles are free of organic contaminants.

22. The thermally conductive compound according to any one of the preceding claims wherein said coupling agent is of the same polarity of said liquid carrier and wherein the percentage of said coupling agent is between 0,5 and 10 percent by weight.

15 23. A thermally conducting compound according to any one of the preceding claims which is used for conducting heat between an electronic component and a heat dissipating means.

24. The thermally conducting compound of Claim 23 wherein said electronic components are semiconductor chips and said heat dissipating means is the cap or an internal thermal enhancement of a semiconductor module.

25 25. The thermally conducting compound of Claim 23 or 24 being in the range of approximately 0,025 to 0,25 mm in thickness.

26. A process for making a thermally conductive compound for conducting heat from electrical components comprising:

20 activating the surface of particles of high thermally conductive material;  
coating said particles with a coupling agent which renders it of comparable polarity to a liquid carrier in which said particles are to eventually be dispersed;  
dispersing said coated particles into a liquid carrier so that a homogeneous compound is formed.

25 27. The process of Claim 26 further comprising the step of adding a polymer to said thermally conductive compound after coating said particles with a coupling agent.

28. The process of Claim 26 or 27 wherein activating the surface of particles is accomplished by thermal treatment and wherein said dispersing is accomplished by high shear milling until a homogeneous compound is formed.

30 29. The process of Claims 26, 27 or 28 further comprising the step of adding fumed silica to said thermally conductive compound.

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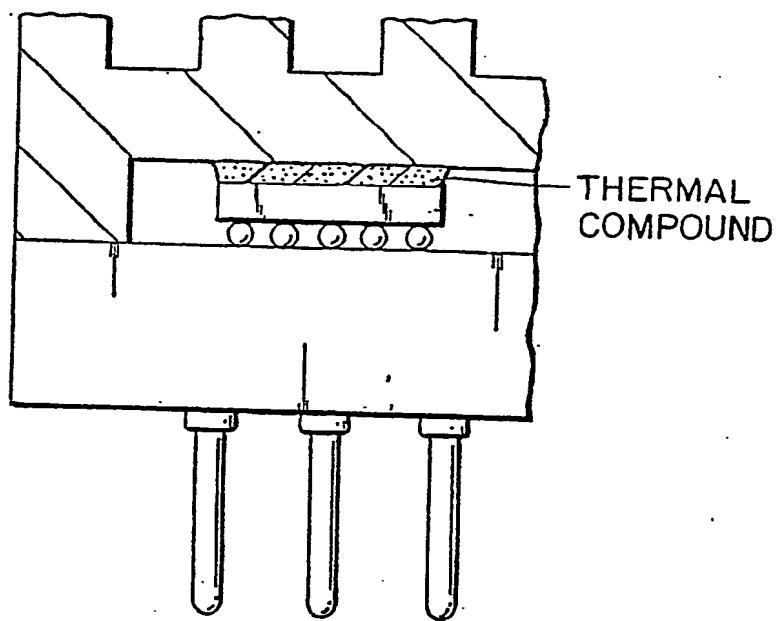


FIG. 1A

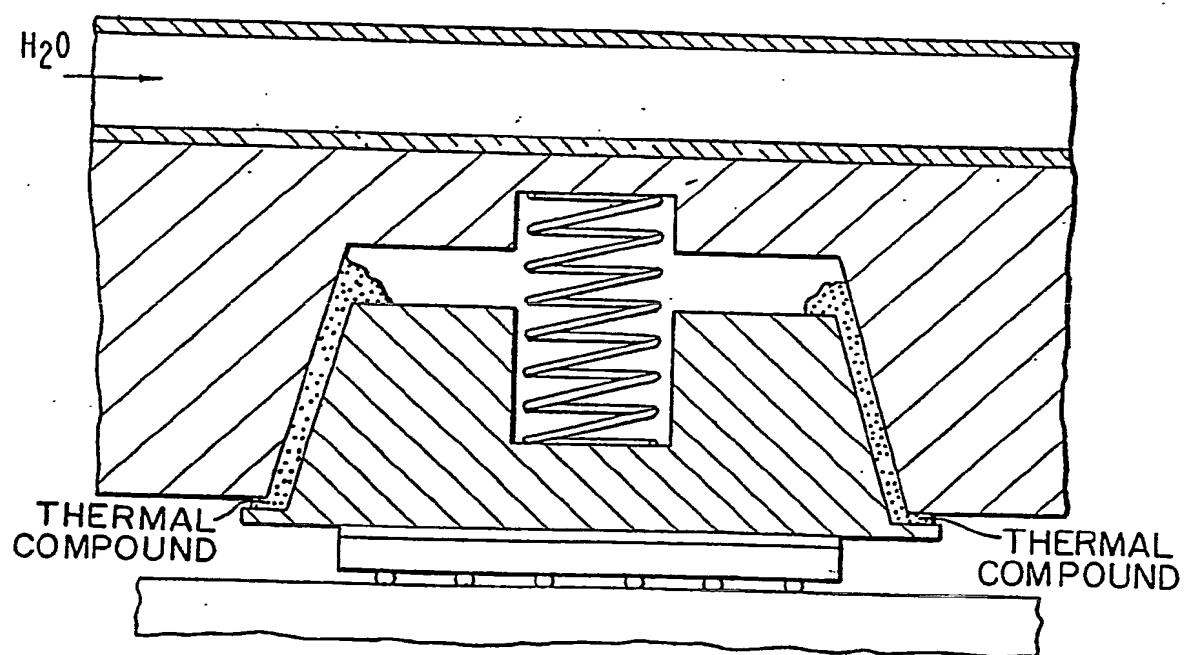
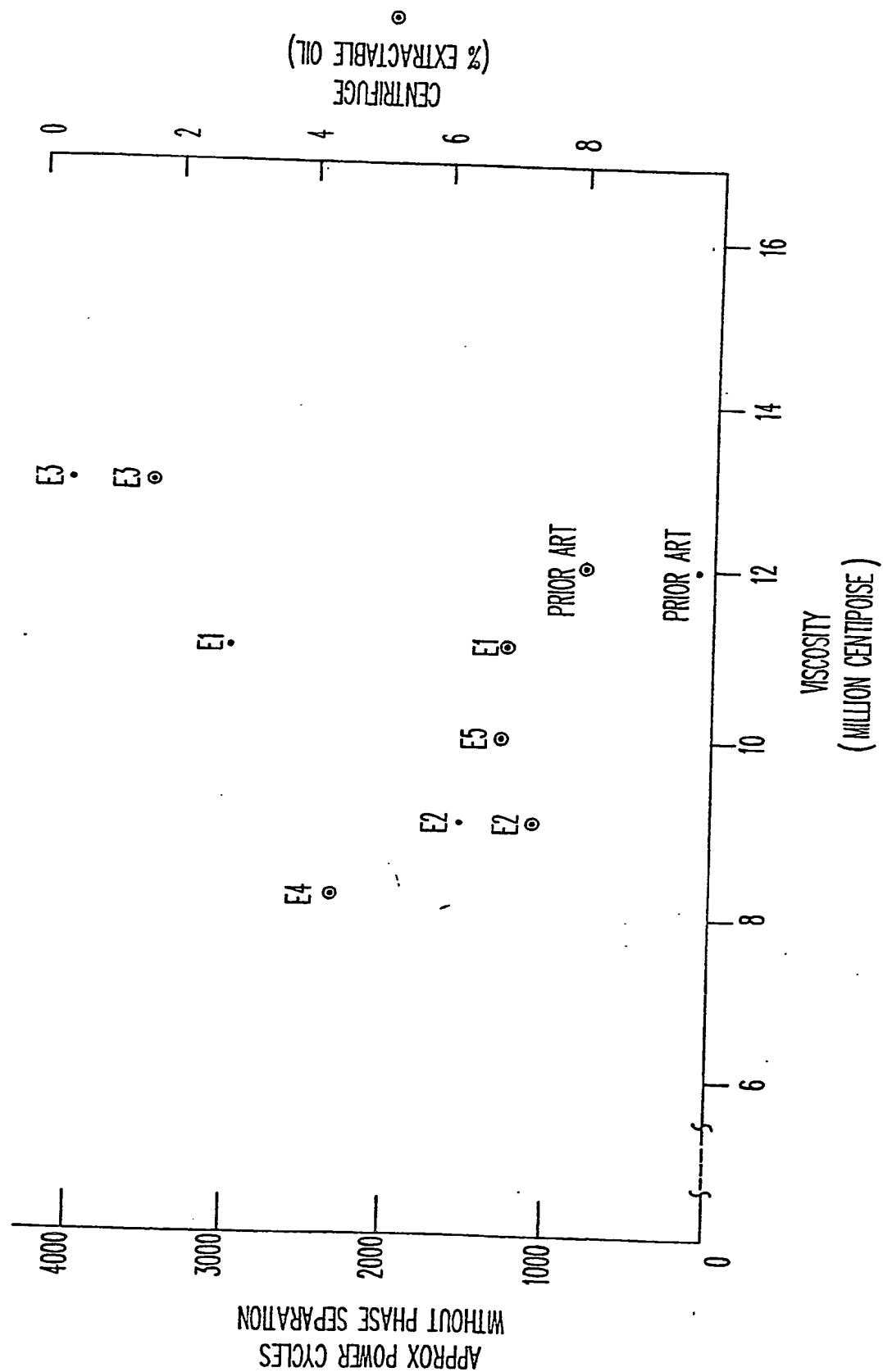


FIG. 1B

FIG. 2



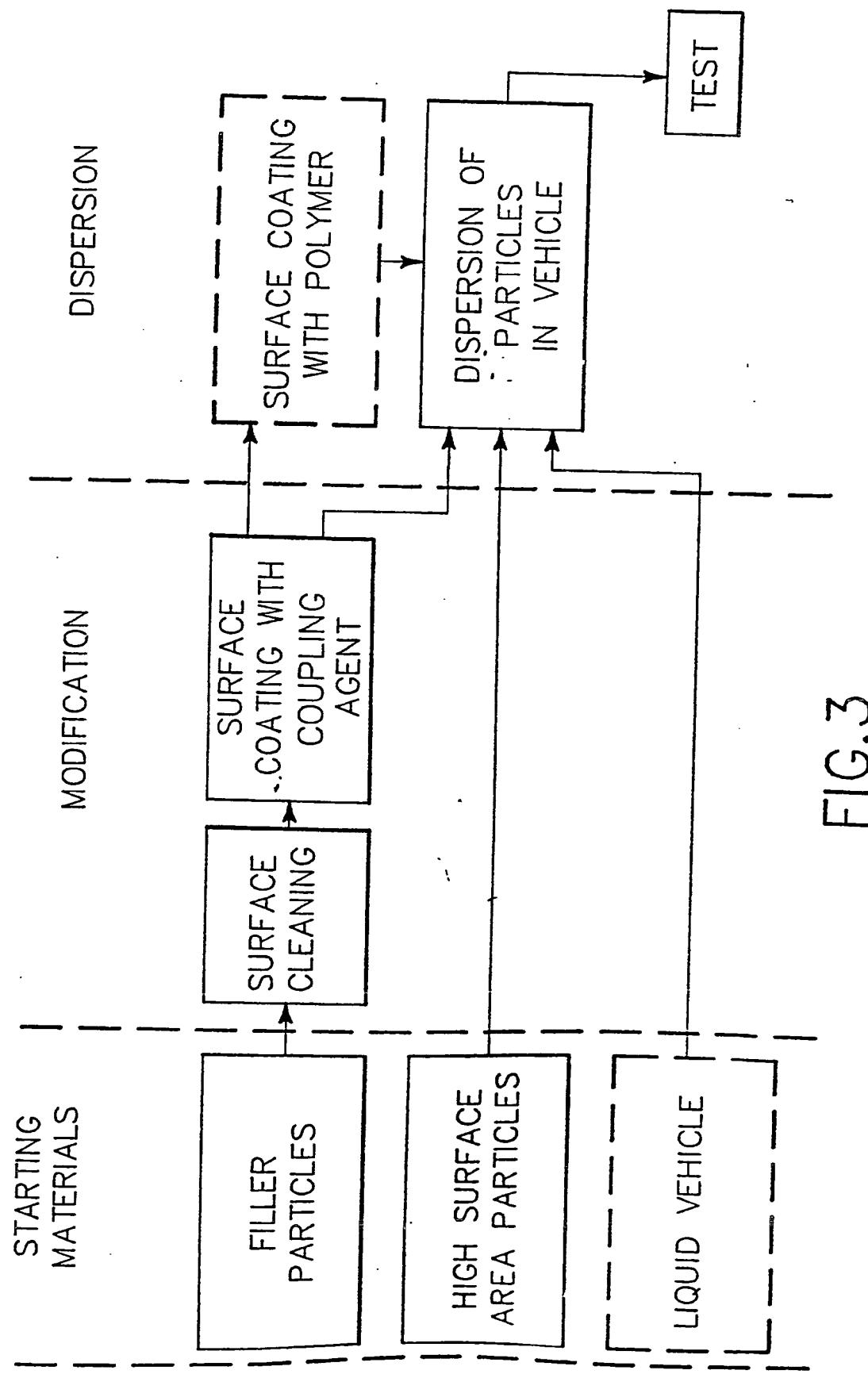


FIG. 3



⑫

## EUROPEAN PATENT APPLICATION

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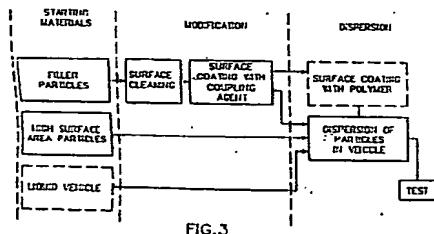
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㉛ Compliant thermally conductive compound.

㉜ A compliant thermally conductive, preferably dielectric, compound that enhances the power dissipation capability of high-powered electrical components such as bipolar VLSI semi-conductor chips. The compound has chemically stable thermal conduction and viscosity properties, is not subject to phase separation during use and may be applied in small gaps to maximize thermal conduction. The compound preferably comprises a liquid carrier having thermal filler particles dispersed therein and a coupling agent having a functionality which is reactive with the calcined surface of the thermal filler particles, and a functionality having preferential wetting of the thermal filler particles over self-condensation. Additional additives such as fumed silica and polyisobutylene enhance the phase stability and resistance to thermo-mechanical shear force degradation of the thermally conductive compound encountered during functional usage, e.g., fluctuating power cycles.





EP 89480042.4

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl 4)						
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim							
A	US - A - 3 885 984 (WRIGHT) * Abstract * --	1	C 09 K 5/00						
D, A	US - A - 3 882 033 (WRIGHT) * Abstract * --	1							
D, A	US - A - 4 265 775 (AAKALU et al.) * Abstract * ----	1							
			TECHNICAL FIELDS SEARCHED (Int. Cl 4)						
			C 09 K 5/00						
<p>The present search report has been drawn up for all claims</p> <table border="1"> <tr> <td>Place of search</td> <td>Date of completion of the search</td> <td>Examiner</td> </tr> <tr> <td>VIENNA</td> <td>23-11-1989</td> <td>LUX</td> </tr> </table> <p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons</p> <p>&amp; : member of the same patent family, corresponding document</p>				Place of search	Date of completion of the search	Examiner	VIENNA	23-11-1989	LUX
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VIENNA	23-11-1989	LUX							



Europäisches Patentamt  
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⑪ Publication number:

0 265 839  
A2

⑫

## EUROPEAN PATENT APPLICATION

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C08K 3/08, C08K 3/22

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⑰ A thermoplastic resin-based molding composition.

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⑰ The thermoplastic polymeric molding composition of the invention has good moldability in shaping by injection molding, extrusion molding and compression molding and capable of giving shaped articles having good machinability in mechanical working such as cutting, grinding and lathing. The composition is compounded from 2 to 70 parts by weight of a thermoplastic polymer such as a polyamide resin and from 98 to 30 parts by weight of a metallic filler such as zinc powder and zinc oxide powder having a surface coated with a water repellent agent such as silane coupling agents, titanate coupling agents and silicone fluids in a specified amount. A part of the above mentioned particulate filler may optionally be replaced with a fibrous filler such as glass fibers and carbon fibers so that the shaped articles of the molding composition may be imparted with increased impact strength.

## A THERMOPLASTIC RESIN-BASED MOLDING COMPOSITION

## BACKGROUND OF THE INVENTION

The present invention relates to a thermoplastic resin-based molding composition or, more particularly, 5 to a molding composition based on a thermoplastic resin as the matrix compounded with a specific filler and suitable for molding various shaped articles used in a wide variety of applications including, for example, structural parts in electric and electronic instruments, industrial machines and transportation machines such as automobiles as well as furnitures and other household commodities.

As is well known, thermoplastic resins have advantages over metallic materials in respect of their good 10 workability, excellent corrosion resistance, lightness in weight and inexpensiveness so that they are useful as a base material for the manufacture of various shaped articles such as structural parts of instruments and machines as well as furnitures and other household commodities.

Thermoplastic resins in general, however, are inferior in the mechanical properties such as tensile strength, impact strength and hardness in comparison with metallic materials and are not quite satisfactory 15 in respect of the heat resistance and dimensional stability. Moreover, the usually advantageous feature of lightness in weight may in some cases cause a disadvantage to give a trifling impression as commercial goods.

A proposal has been made to solve the above described problems by compounding a thermoplastic resin with a metallic filler. For example, thermoplastic resins such as polypropylene, polyethylene, 20 polyamide, poly(ethylene terephthalate), poly(butylene terephthalate) and the like are compounded with a fine powder of a metal such as zinc, copper, iron and the like as a filler to give a resin-based composite molding compound.

Shaped articles prepared from such a metal-filled molding compound, however, more or less have an 25 unavoidable serious problem of rusting of the metal particles contained in the shaped article to cause poor appearance or degradation in the mechanical properties when the article is prolongedly kept in humid air, water, soil or other corrosive environment. When rusting occurs in the molding compound before molding, which is usually in the form of pellets, moreover, drawbacks, are sometimes caused in the molding work of such a deteriorated molding compound.

Several methods have been proposed to solve this problem including a method of forming a corrosion-resistant coating layer of, for example, a rust inhibitor, metal plating and ceramic on the surface of the 30 shaped article, a method of forming a relatively thick uniform skin layer of a rust-free resin on the surface of the shaped article and a method of wrapping the shaped article with a film of a plastic resin having a small permeability to moisture.

These methods, however, cannot provide a complete solution of the problem. For example, the 35 corrosion-resistant coating layer formed on the surface of a shaped article has a problem of inherently low durability because the coating layer gradually falls off the surface in the lapse of time. In addition, the productivity of shaped articles must decrease because the process is complicate for forming such a protective surface layer. The method of forming a skin layer is particularly defective when the shaped article has an irregular configuration or non-uniform wall thickness due to the extreme difficulty in obtaining a skin 40 layer of uniform thickness. The productivity of course cannot be high enough. The method of wrapping with a plastic film also suffers low productivity due to the complicate and troublesome process if not to mention the limited applicability of the method.

In addition to the above described problem due to rusting of metal particles, conventional metallic filler-loaded composite molding compounds have problems in the moldability of the compound and stability of 45 the shaped articles therefrom, especially, when the molding compound has a density in excess of 1.5 g/cm<sup>3</sup> or, in particular, 2.0 g/cm<sup>3</sup>. The moldability of such a molding compound is poor so that the appearance of the articles shaped therefrom is sometimes not quite acceptable. Moreover, the shaped articles of such a molding compound usually have relatively low mechanical strengths or, in particular, impact strength and exhibit a large molding shrinkage sometimes with different ratios of shrinkage between directions. Therefore, it is a rather difficult matter to obtain a satisfactory shaped article of high density with good 50 dimensional stability exhibiting no warping distortion from such a metallic filler-loaded molding compound.

Further, degradation of the matrix resin may sometimes take place in such a metallic filler-loaded composite molding compound due to the influence of the metal particles. The molding compound is also not quite satisfactory as a moldable electroconductive material because sufficiently high electroconductivity can hardly be obtained or the reproducibility of the conductivity, if obtained, is usually low.

## SUMMARY OF THE INVENTION

An object of the present invention therefore is to provide a novel thermoplastic resin-based molding composition loaded with a metallic filler free from the above described problems and disadvantages in the conventional metallic filler-loaded molding compounds. Namely, the molding composition of the present invention should have good moldability and be capable of giving shaped articles having good appearance and high mechanical properties as well as dimensional stability, electroconductivity and resistance against rusting and also suitable for secondary machining such as cutting, grinding and lathing using standard machine tools.

As a result of the extensive investigations undertaken with the above mentioned object, it has been unexpectedly discovered that the problems can be solved by compounding a thermoplastic resin with a specific amount of a metallic filler after a surface treatment of the particles with a specific amount of a compound belonging to the class of so-called water repellent agents, optionally, with further admixture of a small amount of a low-molecular oxidized poly propylene.

Thus, the thermoplastic resin-based molding composition of the present invention comprises:

- (A) from 2 to 70 parts by weight of a thermoplastic polymer as the matrix phase; and
- (B) from 98 to 30 parts by weight of a metallic filler, of which the particles have a surface coated with a water repellent agent, the amount of the water repellent agent being in the range from 0.01 to 5% or, preferably, from 0.3 to 3% by weight based on the metallic filler before coating therewith.

When the molding composition is additionally admixed with (C) a low-molecular oxidized polypropylene, the composition comprises:

- (A) from 2 to 70 parts by weight of a thermoplastic polymer;
- (B) from 98 to 30 parts by weight of a metallic filler, of which the particles have a surface coated with a water repellent agent, the amount of the water repellent agent being as mentioned above; and
- (C) a low-molecular oxidized polypropylene in an amount in the range from 0.1 to 2% by weight based on the total amount of the components (A) and (B).

Although the above mentioned metallic filler is usually in a particulate form, it is sometimes advantageous that a part of such a particulate filler is replaced with a fibrous filler. Namely, the metallic filler as the component (B) in the above given formulations should be a combination of a particulate metallic filler having an average particle diameter, for example, in the range from 0.1 to 20  $\mu\text{m}$  and a fibrous metallic filler having a fiber diameter in the range from 0.03 to 60  $\mu\text{m}$  or, preferably, from 0.1 ~ 20  $\mu\text{m}$  and an aspect ratio in the range from 50 to 2500 in a weight ratio not exceeding 1:1 or, preferably, in the range from 1:1 to 30:1.

## 35 DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The component (A) to form the matrix phase of the inventive molding composition is a thermoplastic polymer which is not limited to a particular type but may be selected from various kinds of thermoplastic resins and elastomers either singly or as a combination of two kinds or more according to need.

The above mentioned thermoplastic resins include polyolefin resins, poly(vinyl chloride) resins, polyamide resins, polyimide resins, polyester resins, polyacetal resins, polycarbonate resins, poly(aromatic ether or thio ether) resins, poly(aromatic ester) resins, polysulfone resins, polystyrene resins, acrylic resins, fluorocarbon resins and the like.

The polyolefin resins include homopolymers and copolymers of  $\alpha$ -olefins such as ethylene, propylene, butene-1, 1-methyl-butene-1, 3-methylpentene-1, 4-methylpentene-1 and the like as well as copolymers of these monomers as the principal ingredient with another monomer of a different type. Typical examples of the polyolefin resins are high-density, medium-density and low-density polyethylenes, straight-chained polyethylenes, super-high molecular polyethylenes, copolymers of ethylene and vinyl acetate and other ethylene-based polymers, atactic, syndiotactic and isotactic polypropylenes, block and random copolymers of propylene and ethylene and other propylene-based polymers, poly(4-methylpentene-1) and the like.

Further, these polyolefins may be modified by the graft polymerization of a polar vinylic monomer such as  $\alpha, \beta$ -unsaturated carboxylic acids and esters thereof exemplified by acrylic acid, esters of acrylic acid, methacrylic acid, esters of methacrylic acid, maleic acid, fumaric acid, citraconic acid, itaconic acid, crotonic acid and the like or an unsaturated epoxide exemplified by glycidyl acrylate, glycidyl methacrylate, vinyl glycidyl ether, allyl glycidyl ether and the like.

The poly(vinyl chloride) resins include homopolymeric poly(vinyl chloride) resins and copolymeric resins of vinyl chloride with another monomer copolymerizable therewith. The copolymeric resins are exemplified by the copolymers of vinyl chloride and an acrylic acid ester, copolymers of vinyl chloride and a methacrylic acid ester, copolymers of vinyl chloride and ethylene, copolymers of vinyl chloride and propylene, copolymers of vinyl chloride and vinyl acetate, copolymers of vinyl chloride and vinylidene chloride and the like. These poly(vinyl chloride) resins may be post-chlorinated to have an increased content of chlorine.

The polyamide resins include 6-nylon, 12-nylon and the like obtained by the ring-opening polymerization of an aliphatic cyclic lactam, 6,6-nylon, 6,10-nylon, 6,12-nylon and the like obtained by the condensation-polymerization of an aliphatic diamine and an aliphatic dicarboxylic acid, condensation-polymerizate of m-xylene and adipic acid and the like obtained by the condensation-polymerization of an aromatic diamine and an aliphatic dicarboxylic acid, condensation-polymerizates of p-phenylene diamine and terephthalic acid or m-phenylene diamine and isophthalic acid and the like obtained by the condensation-polymerization of an aromatic diamine and an aromatic dicarboxylic acid, 11-nylon and the like obtained by the condensation-polymerization of an amino acid, and so on.

The polyimide resins include polyimides and polyamideimides. Exemplary of the polyimides are those obtained from the combinations of pyromellitic anhydride and diamino diphenyl ether, 3,4,3',4'-benzophenone tetracarboxylic acid anhydride and diamino diphenyl ether, bismaleimide and diamino diphenyl methane and the like. Exemplary of the polyamideimides are those obtained from the combination of trimellitic anhydride and diamino diphenyl ether and the like.

The polyester resins include those obtained by the condensation-polymerization of an aromatic dicarboxylic acid and an alkylene glycol exemplified by poly (ethylene terephthalates), poly (methylene terephthalates) and the like.

The polyacetal resins are exemplified by the homopolymeric polyoxymethylenes and copolymers of formaldehyde and ethylene oxide obtained from trioxane and ethylene oxide.

Preferable examples of the polycarbonate resins are the 4,4'-dihydroxy diallyl alkane-based polycarbonates and the bisphenol A-based polycarbonates prepared by the phosgene method, in which bisphenol A and phosgene are reacted, or the ester interchange method, in which bisphenol A and a diester of carbonic acid such as diphenyl carbonate are reacted. Usable polycarbonate resins include those modified or flame-retardant bisphenol A-based polycarbonates obtained by partially replacing the bisphenol A in the above mentioned preparation of unmodified polycarbonates with 2,2-bis(4-hydroxy-3,5-dimethyl phenyl) propane, 2,2-bis(4-hydroxy-3,5-dibromo phenyl) propane and the like.

The poly(aromatic ether or thioether) resins have ether linkages or thioether linkages in the polymeric molecular chain and are exemplified by polyphenylene oxides, styrene-grafted polyphenylene oxides, polyphenylene sulfides and the like.

The poly(aromatic ester) resins are exemplified by polyoxybenzoyls obtained by the condensation-polymerization of 4-hydroxy benzoic acid and polyarylates obtained by the condensation-polymerization of bisphenol A and an aromatic dicarboxylic acid such as terephthalic acid and isophthalic acid.

The polysulfone resins have sulfone linkages in the polymeric molecular chain and are exemplified by polysulfones obtained by the condensation-polymerization of bisphenol A 4,4'-dichlorodiphenyl sulfone, polyether sulfones having a structure in which phenylene groups are bonded together at the 1,4-positions through ether linkages and sulfone linkages and polyaryl sulfones having a structure in which diphenylene groups and diphenylene ether groups are alternately bonded together through sulfone linkages.

The polystyrene resins include homopolymers of styrene and  $\alpha$ -methyl styrene and copolymers thereof as well as copolymers of them as the principal ingredient with another monomer copolymerizable therewith. Typical examples of the polystyrene resins are general-purpose polystyrenes, high-impact polystyrenes, heat-resistant polystyrenes, polymers of  $\alpha$ -methyl styrene, copolymers of acrylonitrile, butadiene and styrene (ABS), copolymers of acrylonitrile and styrene (AS), copolymers of acrylonitrile, chlorinated polyethylene and styrene (ACS), copolymers of acrylonitrile, ethylenepropylene rubber and styrene (AES), copolymers of acrylic rubber, acrylonitrile and styrene and the like.

The acrylic resins include polymers of acrylic acid esters and methacrylic acid esters exemplified by methyl, ethyl, n-propyl, isopropyl and butyl esters of acrylic acid and methacrylic acid. Particularly preferable among them are poly(methyl methacrylate) resins from the standpoint of practically using the inventive molding composition as an industrial material.

The fluorocarbon resins include homopolymers of tetrafluoro ethylene, hexafluoro propylene, vinylidene fluoride, vinyl fluoride and the like and copolymers thereof as well as copolymers of these fluorinated monomers as the principal ingredient with another monomer copolymerizable therewith. Exemplary of the fluorocarbon resins are poly(tetrafluoroethylenes), poly(vinylidene fluorides), poly(vinyl fluorides), 5 copolymers of tetrafluoroethylene and ethylene, copolymers of tetrafluoroethylene and vinylidene fluoride, copolymers of hexafluoropropylene and vinylidene fluoride, copolymers of tetrafluoroethylene, hexafluoropropylene and vinylidene fluoride and the like.

The elastomeric polymers suitable as the component (A) include natural rubber and various kinds of synthetic rubbers exemplified by polybutadiene rubbers (BR), copolymeric rubbers of styrene and butadiene (SBR), copolymeric rubbers of acrylonitrile and butadiene (NBR), copolymeric rubbers of styrene, butadiene and acrylonitrile, polychloroprene rubbers (CR) and other butadiene-based rubbers, polyisoprene rubbers or synthetic natural rubbers, copolymeric rubbers of isobutylene and isoprene or so-called butyl rubbers (IIR), copolymeric rubbers of acrylonitrile and isoprene, polyisobutylene rubbers, copolymeric rubbers of ethylene and propylene, copolymeric rubbers of ethylene and vinyl acetate, chlorinated polyethylenes, chlorosulfonated polyethylenes, urethane rubbers, silicone rubbers, fluorocarbon rubbers, acrylic rubbers, epichlorohydrin rubbers, propylene oxide rubbers, polyester-based elastomers, 15 polyacrylate-based elastomers, polyolefin-based elastomers, poly(vinyl chloride)-based elastomers, copolymeric elastomers of styrene and butadiene, polystyrene-based elastomers, polyamide-based elastomers, polyurethane-based elastomers and the like.

20 The above named polymers can be used either singly or as a mixture of two kinds or more according to need as the component (A) to form the matrix phase of the inventive molding composition. Particularly preferable among them are polyamide resins such as 6-nylon, 6,6-nylon, 12-nylon and the like, polypropylenes and poly(butylene terephthalates).

The component (B) to form the disperse phase in the inventive molding composition is a metallic filler 25 usually in a particulate form. Metals of which the powder as the metallic filler is prepared include zinc, copper, iron, lead, aluminum, nickel, chromium, titanium, manganese, tin, platinum, tungsten, gold, magnesium, cobalt, strontium and the like as well as alloys of these metallic elements such as stainless steel, solder alloys, brass, bronze and the like, of which zinc is particularly preferred. Zinc oxide also can be used. Certain ceramic materials obtained in a powdery form can be used as the filler including silicon carbide, 30 silicon nitride, zirconia, aluminium nitride, titanium carbide and the like.

The metallic filler in a particulate form as the component (B) should have an average particle diameter in the range from 0.2 to 20  $\mu\text{m}$  or, preferably, in the range from 0.4 to 10  $\mu\text{m}$ . When the filler particles are too fine, the molding composition compounded with the filler may be poor in the moldability. When the filler particles are too coarse, on the other hand, the molding composition compounded with the filler cannot give 35 a shaped article having a sufficiently high impact strength and free from the drawbacks of warping distortion after molding.

When a particularly high impact strength is desired of the shaped article of the inventive molding composition, it is advantageous to replace a part of the above described filler in a particulate form with a fibrous filler. Suitable fibrous fillers include inorganic fibers such as glass fibers, carbon fibers, magnesium 40 sulfate fibers and the like, fibers and whiskers of a metal such as stainless steel, brass, aluminum, nickel and the like, whiskers of ceramics such as potassium titanate, silicon carbide and the like, and organic fibers such as aromatic polyamide fibers, cellulosic fibers, nylon fibers, polyester fibers, polypropylene fibers and the like. Preferable among them are glass fibers, carbon fibers, stainless steel fibers, brass fibers, potassium titanate whiskers, aromatic polyamide fibers and the like. Glass fibers are particularly 45 preferred. These fibrous fibers can be used either singly or as a combination of two kinds or more according to need.

The fibers of the fibrous filler should have a fiber diameter in the range from 0.03 to 60  $\mu\text{m}$  or, preferably, from 0.1 ~ 20  $\mu\text{m}$  and an aspect ratio in the range from 50 to 2500 or, preferably, from 100 to 50 2000. When the aspect ratio of the fibers is too small, desired improvement in the impact strength of the shaped article cannot be achieved as desired. When the aspect ratio of the fibers is too large, on the other hand, the shaped articles of the molding composition may be subject to an increased molding shrinkage and drawbacks of warping distortion after molding so that the molding composition cannot be used industrially due to the poor dimensional stability of the shaped articles therefrom.

When a particulate filler and a fibrous filler are used in combination as the component (B) in the 55 inventive molding composition, the weight ratio of them should not exceed 1:1 although no substantial improvement can be obtained in the impact strength of the shaped articles molded of the composition when the amount of the fibrous filler is too small. In this regard, the weight ratio of the particulate to fibrous fillers should be in the range from 1:1 to 30:1 or, preferably, from 2:1 to 20:1.

When the inventive molding composition is prepared by compounding the thermoplastic polymer as the component (A) with the filler as the component (B), it is essential that the filler is subjected in advance to a surface treatment with a water repellent agent in a specific amount. Suitable water repellent agents include silane-based coupling agents, titanate-based coupling agents, silicone fluids, higher fatty acids, higher alcohols, waxes and the like, of which silane-based coupling agents, titanate-based coupling agents and silicone fluids are preferred. These water repellent agents can be used either singly or as a combination of two kinds or more according to need.

The type of the above mentioned silane-based coupling agent is not particularly limitative, and any of known ones can be used. Exemplary of suitable silane-based coupling agents are triethoxy silane, vinyl tris(β-methoxyethoxy) silane, 3-methacryloxypropyl trimethoxy silane, 3-glycidyloxypropyl trimethoxy silane, 2-(3,4-epoxycyclohexyl)ethyl trimethoxy silane, N-(2-aminoethyl)-3-aminopropyl methyl dimethoxy silane, N-(2-aminoethyl)-3-aminopropyl methyl dimethoxy silane, 3-aminopropyl triethoxy silane, N-phenyl-3-aminopropyl trimethoxy silane, 3-mercaptopropyl trimethoxy silane, 3-chloropropyl trimethoxy silane and the like, of which 3-aminopropyl triethoxy silane and N-(2-aminoethyl)-3-aminopropyl trimethoxy silane are preferred.

The type of the above mentioned titanate-based coupling agents is also not particularly limitative and any of hitherto known ones can be used. Exemplary of suitable titanate-based coupling agents are isopropyl triisostearoyl titanate, isopropyl tri(dodecylbenzene sulfonyl) titanate, isopropyl tris(dioctyl pyrophosphato) titanate, tetraiso propyl bis(dioctylphosphito) titanate, tetraoctyl bis(ditridecyl phosphito) titanate, tetra(2,2-diallyloxy methyl-1-butyl) bis(di-tridecyl phosphito) titanate, bis(dioctyl pyrophosphato) oxyacetate titanate, bis(dioctyl pyrophosphato) ethylene titanate, isopropyl trioctanoyl titanate, isopropyl dimethacryl isostearoyl titanate, isopropyl tri(dioctyl phosphato) titanate, isopropyl tri(cumyl phenyl) titanate, isopropyl tri(N-amidoethyl aminoethyl) titanate, dicumyl phenyl oxyacetate titanate, di(isostearoyl) ethylene titanate and the like, of which isopropyl triisostearoyl titanate and isopropyl tri(N-amidoethyl aminoethyl) titanate are preferred.

Further, suitable silicone fluids include dimethyl silicone fluids, methyl phenyl silicone fluids, polyether-modified silicone fluids, alkyl-modified silicone fluids, methyl hydrogen polysiloxane fluids and the like, of which dimethyl silicone fluids and methyl hydrogen polysiloxane fluids are preferred.

To summarize the description on the types of the water repellent agents, dimethyl silicone fluids, methyl hydrogen polysiloxane fluids and 3-aminopropyl triethoxy silane are particularly preferable as the surface treatment agent of the filler as the component (B) in the inventive molding composition.

The procedure for the surface treatment of the component (B) with the water repellent agent is not particularly limitative according to any known method conventionally undertaken for the surface treatment of a powdery material. A preferable method in respect of the versatility and controllability of the temperature and mixing velocity in the treatment is to use a Henschel mixer in which the water repellent agent is sprayed on to the filler under agitation and thoroughly mixed together.

The water repellent agent in this surface treatment of the filler as the component (B) should be used in an amount in the range from 0.01 to 5% by weight or, preferably, from 0.05 to 3% by weight or, more preferably, from 0.1 to 2% by weight based on the amount of the filler as the component (B) before the surface treatment. When the amount of the water repellent agent is too small, no sufficient coupling effect can be exhibited between the surface of the filler and the matrix phase so that the resultant molding composition would be poor in the moldability. When the amount thereof is too large, on the other hand, a phenomenon of slipping may be caused due to the excessively strong effect of lubrication between the filler surface and the matrix phase leading to disadvantages of decreased productivity of pelletization of the molding composition and decreased workability in the molding works along with a problem of poor appearance of the shaped articles prepared from the composition as a result of strong bleeding of the water repellent agent on the surface of the shaped article.

The fillers thus surface-treated or coated with the water repellent agent as the component (B) can be used either singly or as a combination of two kinds or more according to need. The compounding amount of the component (B) in the inventive molding composition should be in the range from 30 to 98 parts by weight or, preferably, from 50 to 97 parts by weight or, more preferably, from 60 to 95 parts by weight per 100 parts by weight of the total amount of the components (A) and (B).

As is mentioned before, the inventive molding composition can be further admixed with a low-molecular oxidized polypropylene as the component (C) in an amount in the range from 0.1 to 2% by weight based on the total amount of the polymeric matrix phase as the component (A) and the filler after the surface treatment as the component (B). The low-molecular oxidized polypropylene is prepared by the oxidative degradation of, for example, an isotactic poly propylene as a solid or melt or in the form of a solution with an oxidizing agent such as peroxides. Carboxyl groups and other types of oxygen-containing groups are

introduced into the molecular structure of the polypropylene by this oxidizing reaction. By virtue of the carboxyl groups introduced into the molecular structure, the low-molecular oxidized polypropylene has increased miscibility with thermoplastic resins having polarity such as polyamides in comparison with non-oxidized low-molecular polypropylenes. It is preferable to use a low-molecular oxidized polypropylene having an average molecular weight in the range from 1500 to 20000. When admixed with an appropriate amount of such a low-molecular oxidized polypropylene, the molding composition is imparted with improved moldability and capable of giving shaped articles having improved mechanical strengths and electric conductivity.

When improvements in the mechanical properties and dimensional stability of shaped articles of the composition are desired, it is sometimes advantageous to admix the composition with a modifier such as a modified polyolefin which serves to increase the affinity between the polymeric matrix as the component (A) and the surface of the filler as the component (B). Suitable polyolefin-based modifiers include, for example, polyethylene and polypropylene modified by graft-polymerization of 0.05 to 20% by weight of a monomer exemplified by unsaturated organic acids and derivatives thereof such as acrylic acid, methacrylic acid, maleic acid, itaconic acid and other organic acids, maleic anhydride, itaconic anhydride, citraconic anhydride and other anhydrides of unsaturated organic acids, methyl acrylate, monomethyl maleate and other esters of unsaturated organic acids, acrylamide, fumaric acid monoamide and other amides of unsaturated organic acids, itaconic acid imide and other imides of unsaturated organic acids, and so on. The modification reaction of the polyolefin by the polymerization of these monomers can be accelerated by an organic peroxide such as benzoyl peroxide, lauroyl peroxide, dicumyl peroxide, tert-butyl hydroperoxide and the like.

Usable modifiers in addition to the above described ones include ethylene- or propylene-based polymers modified by graft polymerization of an unsaturated epoxide such as glycidyl acrylate, glycidyl methacrylate, vinyl glycidyl ether, allyl glycidyl ether and the like carried out optionally with admixture of a liquid rubber such as a polybutadiene hydroxylated at the molecular chain ends.

The amount of these modifiers added to the inventive molding composition should usually be in the range from 1 to 10% by weight based on the total amount of the components (A) and (B). When the amount thereof is too small, the desired improvement by the addition of the modifier cannot be fully exhibited as a matter of course. When the amount thereof is too large, on the other hand, phase separation may sometimes take place in the shaped article of the composition to greatly decrease the mechanical strengths.

It is optional according to need that the molding composition of the invention is further admixed with various kinds of inorganic and organic fillers though in a limited amount not to substantially affect the desirable properties of the composition or the shaped article prepared therefrom. Such an optional filler may be powdery, granular or fibrous.

Inorganic fillers suitable for the above mentioned optional addition are exemplified by oxides such as silica, diatomaceous earth, barium ferrite, beryllium oxide, pumice, pumice balloons and the like, hydroxides such as aluminum hydroxide, magnesium hydroxide, basic magnesium carbonate and the like, carbonates such as calcium carbonate, magnesium carbonate, dolomite, dawsonite and the like, sulfates and sulfites such as calcium sulfate, barium sulfate, ammonium sulfate, calcium sulfite and the like, silicates such as talc, clay, mica, asbestos, glass balloons, glass beads, montmorillonite, bentonite and the like, carbonaceous fillers such as carbon black, graphite powder, carbon balloons and the like, molybdenum sulfide, zinc borate, barium metaborate, calcium borate, sodium borate and the like. These inorganic fillers can be used either singly or as a combination of two kinds or more according to need.

Organic fillers suitable for the above mentioned optional addition are exemplified by non-fibrous ones such as rice hulls, wood flour, fragments of paper and cellophane and the like. These organic fillers also can be used either singly or as a combination of two kinds or more according to need. It is of course optional that inorganic and organic fillers are used in combination.

If desired, the molding composition of the invention can be admixed with various kinds of additives conventionally compounded in resin-based molding compositions including, for example, lubricants, coloring agents, stabilizers, antioxidants, ultraviolet absorbers, antistatic agents, flame retardant agents, plasticizers, blowing agents and the like according to the intended application of the articles shaped from the molding composition.

The molding composition of the present invention can be prepared by uniformly blending and compounding the components (A) and (B), optionally, together with the component (C) and above described optional additives in a conventional procedure of kneading in a molten condition by using a suitable blending machine such as Henschel mixers, single- or double-screw extruder machines, Banbury mixers, roller mixers and the like, of which Henschel mixers, extruder machines and Banbury mixers are preferred.

The molding composition of the present invention can be shaped into articles by any conventional molding method such as injection molding, extrusion molding, compression molding and the like without particular limitations by virtue of the good moldability. The composition can give not only shaped articles having complicated configuration as molded but also shaped articles suitable for secondary working to

5 meet various applications by adequately modifying the blending ratio of the components. The application fields of the shaped articles of the inventive molding composition include structural and functional parts in electric and electronic instruments, machines in general, automobiles and the like, furnitures, household commodities and so on. Particularly exemplary of the shaped articles are, for example, all kinds of rotatory members for power transmission such as flywheels, gears, pulleys, cams, motors and the like, housings, 10 chassis, turn tables and the like of record players, cassette tape recorders, speaker boxes, etc., sound insulating and shielding materials, vibration damping materials, shielding materials for electro-magnetic waves, furnitures, kitchenwares, office supplies, toys, fishing implements and so on.

The thermoplastic resin-based molding composition of the present invention is prepared by compounding a thermoplastic polymer as the matrix phase with a metallic filler after a surface treatment with a water repellent agent so that the filler particles dispersed in the polymeric matrix are highly resistant against rusting along with greatly improved affinity between the surface of the filler particles and the matrix polymer. Accordingly, the inventive molding composition has good moldability and is capable of giving shaped articles having outstandingly good outer appearance, excellent mechanical properties, high dimensional stability without warping distortion and stable electric conductivity. By virtue of the improved 20 moldability, the inventive molding composition can be shaped into articles having large dimensions or a complicated configuration and the shaped articles have good secondary workability suitable for machining with standard machine tools such as cutting, grinding, lathing and the like. Thus, present invention provides a material having excellent moldability into shaped articles and machinability of the shaped articles in combination. Such a combination of moldability and machinability is the very great advantage of the 25 inventive molding composition never obtained in any of conventional resin-based molding compositions and metals.

In the following, examples are given to illustrate the inventive molding compositions in more detail but not to limit the scope of the invention in any way.

In the examples given below, the polymeric materials used as the polymeric matrix of the molding 30 compositions include the commercially available products listed below, each of which is referred to hereinbelow with the abridged symbol of the name preceding the name of the polymeric material.

- (1) 6-PA: 6-nylon, LM-102, a product by Kanegafuchi Chemical Industry Co.
- (2) 66-PA: 6,6-nylon, 1200S, a product by Asahi Chemical Industry Co.
- (3) 12-PA: 12-nylon, 3014U, a product by Ube Kosan Co.
- 35 (4) MXDA: polyamide, 6002, a product by Mitsubishi Gas Chemical Co.
- (5) PP: polypropylene, J2000G, a product by Idemitsu Petrochemical Co.
- (6) PBT: poly(butylene terephthalate), 5010, a product by Mitsubishi Chemical Industries Co.
- (7) PET: poly(ethylene terephthalate), MA 2101, a product by Unitika Co.
- (8) POM: polyacetal, 3010, a product by Asahi Chemical Industry Co.
- 40 (9) PS: polystyrene, HT-53, a product by Idemitsu Petrochemical Co.
- (10) PE: polyethylene, 110J, a product by Idemitsu Petrochemical Co. having a melt index of 14 g/10 minutes

(11) ABS: copolymeric resin of acrylonitrile, butadiene and styrene, JSR-35, a product by Japan Synthetic Rubber Co.

- 45 (12) PC: polycarbonate, N-2500, a product by Idemitsu Petrochemical Co.
- (13) PVC: poly(vinyl chloride), JZ-102F, a product by Shin-Etsu Polymer Co.
- (14) PMMA: poly(methyl methacrylate), 50N, a product by Asahi Chemical Industry Co.
- (15) PPO: poly(phenylene oxide), 731J, a product by Engineering Plastics Co.
- (16) PSO: polysulfone, P-1700, a product by Nissan Chemical Co.
- 50 (17) PI: polyimide, SP-1, a product by DuPont Far East Co.
- (18) SBR: styrene-butadiene rubber, JSR-1500, a product by Japan Synthetic Rubber Co.
- (19) EPR: ethylene-propylene copolymeric rubber, EP-07P, a product by Japan Synthetic Rubber Co.
- (20) SR: silicone rubber, KE-931U, a product by Shin-Etsu Chemical Co.
- (21) EVA: ethylene-vinyl acetate copolymeric rubber, Evatake D-3021, a product by Sumitomo Chemical Co.
- 55 (22) PEE: polyester-based elastomer, Belprene P-40B, a product by Toyo Spinning Co.
- (23) POE: polyolefin-based elastomer, TPE-1500, a product by Sumitomo Chemical Co.

Further, in the following examples, various kinds of fillers were used as listed below.

- (1) Zn: zinc powder having an average particle diameter of about 3  $\mu\text{m}$ , a product by Sakai Chemical Co.
- (2) ZnO: zinc oxide having an average particle diameter of about 3  $\mu\text{m}$ , a product by Sakai Chemical Co.
- 5 (3) Cu: copper powder having an average particle diameter of about 5  $\mu\text{m}$ , a product by Fukuda Kinzoku Hakufun Kogyo Co.
- (4)  $\alpha$ -Fe: iron powder having an average particle diameter of about 0.5  $\mu\text{m}$ , a product by Dowa Teppun Kogyo Co.
- 10 (5)  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>: iron oxide powder having an average particle diameter of about 0.5  $\mu\text{m}$ , a product by Dowa Teppun Kogyo Co.
- (6) Ni: nickel powder having an average particle diameter of about 3  $\mu\text{m}$
- (7) Pb: lead powder having an average particle diameter of 10  $\mu\text{m}$
- (8) Al: aluminum powder having an average particle diameter of about 10  $\mu\text{m}$
- 15 (9) Sn: tin powder having an average particle diameter of about 7  $\mu\text{m}$
- (10) SnO<sub>2</sub>: tin oxide powder having an average particle diameter of about 3  $\mu\text{m}$
- (11) SS: stainless steel powder having an average particle diameter of about 10  $\mu\text{m}$
- (12) SA: powder of solder alloy having an average particle diameter of about 8  $\mu\text{m}$
- (13) BR: brass powder having an average particle diameter of about 10  $\mu\text{m}$
- 20 (14) SF: stainless steel fibers having a diameter of 10  $\mu\text{m}$  and fiber length of 6 mm
- (15) NF: nickel fibers having a diameter of 10  $\mu\text{m}$  and fiber length of 8 mm
- (16) PT: whiskers of potassium titanate having a diameter of 0.3  $\mu\text{m}$  and length of 15  $\mu\text{m}$
- (17) ZrO<sub>2</sub>: zirconia powder having an average particle diameter of about 0.5  $\mu\text{m}$

The above listed fillers were used each after a surface treatment with one of the water repellent agents shown below.

- 25 A: 3-aminopropyl triethoxy silane, a product by Nippon Unicar Co.
- B: N-(2-aminoethyl)-3-aminopropyl trimethoxy silane, a product by Nippon Unicar Co.
- C: methyl hydrogen polysiloxane fluid, a product by Shin-Etsu Chemical Co.
- D: dimethyl silicone fluid, a product by Shin-Etsu Chemical Co.
- E: isopropyl triisostearoyl titanate, a product by Ajinomoto Co.
- 30 F: isopropyl tri(N-amidoethyl aminoethyl) titanate, a product by Ajinomoto Co.
- G: finely divided silica powder having an average particle diameter of about 12  $\mu\text{m}$ , a product by Nippon Aerosil Co.
- H: finely divided silica powder having an average particle diameter of about 7  $\mu\text{m}$ , a product by Nippon Aerosil Co.
- 35 I: stearic acid
- J: stearyl alcohol
- K: polyethylene wax

40 Example 1.

A 0.3 part by weight of 3-aminopropyl triethoxy silane was sprayed to 100 parts by weight of a zinc powder having an average particle diameter of 3  $\mu\text{m}$  contained in a Henschel mixer of 20 liter capacity and the mixer was run for 5 minutes at a velocity of 1000 rpm to mix them together at a temperature of 60 to 100 °C to prepare a surface-coated zinc powder. Thereafter, a 6-PA resin in an amount of 50% by weight based on the surface-coated zinc powder was added to the mixer and melted and mixed together by running the mixer for 15 minutes at a velocity of 2000 rpm and at a temperature of 200 to 300 °C to give a composite molding resin composition with further admixture of 0.3% by weight of an antioxidant (Irganox 1010, a product by Ciba Geigy Co.), 0.3% by weight of calcium stearate as a lubricant (a product by Nippon Yushi Co.) and 1.0% by weight of carbon black (DL-600, a product by Lion Akzo Co.), each amount being based on the total amount of the 6-PA resin and the surface-coated zinc powder.

The thus obtained molding composition was pelletized by using a single-screw extruder machine (Model NVC-50, manufactured by Nakatani Machinery Co.) operated at a temperature of 200 to 300 °C with a rate of extrusion of 30 kg/hour and the pellets were shaped into test plates by injection molding using an injection molding machine (Model FS-160S, manufactured by Nissei Resin Industry Co.) at a temperature of 200 to 300 °C.

The test plates were subjected to the evaluation of various properties including the following items each according to the procedure described below. The results are shown in Table 1.

## (1) Resistance against rusting

5 A test plate of 75 mm by 75 mm wide and 3.2 mm thick was put into a bag made of a polyethylene film of 40  $\mu\text{m}$  thickness and, after sealing of the opening by welding, the bag was heated for 100 hours or 300 hours in an atmosphere of 95% relative humidity at 60  $^{\circ}\text{C}$ . The test plate taken out of the bag was inspected for the surface condition with naked eyes or by using a magnifying lens of 25 magnification to give the results in four ratings of A, B, C and D according to the following criteria.

10 A: no rust found under magnifying lens  
 B: powder-like rust found under magnifying lens  
 C: small number of rust speckles found with naked eyes  
 D: large number of rust speckles found with naked eyes

## (2) Moldability

15 A box having outer dimensions of 150 mm by 80 mm by 80 mm with a wall thickness of 5 mm was shaped from the molding composition by injection molding using the same injection molding machine as used in the preparation of the test plates above to determine the critical impregnation pressure or minimum impregnation pressure for short shot in kg/cm<sup>2</sup>. The thus molded boxes were visually inspected for the 20 outer appearance and the results were expressed in three ratings of A, B and C according to the following criteria.

25 A: beautiful and acceptable  
 B: small number of silver marks found  
 C: large number of silver marks found

## (3) Izod impact strength

30 Measurement was performed according to ASTM D-1302 to give the results in kg cm/cm.

## (4) Electric resistance

35 Measurement was performed according to JIS C 1302 by using an automatic insulation-resistance tester (Model F-535F, manufactured by Fuso Electric Co.) with a voltage impression of 500 volts DC to give the total resistance in megaohm.

40 Examples 2 to 65 and Comparative Examples 1 to 6.

45 The experimental procedure in each of these Examples and Comparative Examples was substantially the same as in Example 1 using the same zinc powder as the filler excepting replacement of the 6-PA resin as the matrix polymer and the 3-aminopropyl triethoxy silane as the water repellent agent each with the material shown in Table 1 in an amount also indicated in the same table. In the formulations shown in Table 50 1, the amounts of the filler and the matrix polymer given in parts by weight are given per 100 parts by weight of the total amount of the filler after the surface treatment and the matrix polymer and the amount of the water repellent agent given in % by weight is based on the amount of the filler before the surface treatment. The molding compositions prepared in Comparative Examples 2 and 4 were disadvantageous in respect of the low productivity in pelletization due to slipping. Table 1 also shows the results of the evaluation of the products carried out in the same manner as in Example 1. In Examples 64 and 65, the zinc powder as the filler and the finely divided silica powder as the water repellent agent were dry-blended in the Henschel mixer operated at a velocity of 1000 rpm for 5 minutes at a temperature of 60 to 100  $^{\circ}\text{C}$  before the addition of the 6-PA resin.

55

Table 1 (Part 1)

Example	Filler (parts by weight)	Water repellent agent (% by weight)	Matrix polymer (parts by weight)	Rust after		Moldability	Izod impact test	Elec- tric resist- ance, mega- ohm
				100 hours	300 hours			
1	Zn (50)	A (0.3)	6-PA (50)	A	A	31	A	10.2
2	Zn (70)	A (0.3)	6-PA (30)	A	A	34	A	8.9
3	Zn (90)	A (0.3)	6-PA (10)	A	A	40	A	7.5
4	Zn (95)	A (0.3)	6-PA (5)	A	A	45	B	5.7
5	Zn (90)	A (1.0)	6-PA (10)	A	A	39	A	7.6
6	Zn (90)	A (3.0)	6-PA (10)	A	A	35	A	7.9
7	Zn (90)	A (0.3)	66-PA (10)	A	A	42	A	7.4
8	Zn (70)	A (0.3)	PP (30)	A	A	34	A	10.0
9	Zn (80)	A (0.3)	PP (20)	A	A	37	A	8.1
10	Zn (95)	A (0.3)	PP (5)	A	A	42	A	7.4
11	Zn (90)	A (0.3)	PBT (10)	A	A	45	A	6.7
12	Zn (90)	A (0.3)	PET (10)	A	A	46	A	6.1
13	Zn (90)	A (0.3)	POM (10)	A	A	43	A	7.7
14	Zn (90)	A (0.3)	PE (10)	A	A	39	A	9.2
15	Zn (90)	A (0.3)	ABS (10)	A	A	41	A	11.4

Table 1 (Part 2)

	Filler (parts by weight)	Water repellent agent (% by weight)	Matrix polymer (parts by weight)	Rust after		Moldability	Izod impact test kg/cm <sup>2</sup>	Elec- tric resist- ance, mega- ohm
				100 hours	300 hours			
Exam- ple	18 Zn (90)	B (0.3)	6-PA (10)	A	A	41	A	6.9
	19 Zn (90)	C (0.05)	6-PA (10)	A	B	49	A	6.7
	20 Zn (90)	C (0.5)	6-PA (10)	A	A	41	A	7.1
	21 Zn (90)	C (2.0)	6-PA (10)	A	A	39	A	7.7
	22 Zn (90)	C (0.5)	PP (10)	A	A	37	A	8.7
	23 Zn (90)	C (0.5)	PBT (10)	A	A	39	A	6.9
	24 Zn (90)	C (0.5)	POM (10)	A	A	37	A	6.9
	25 Zn (90)	C (0.5)	ABS (10)	A	A	37	A	11.7
	44 Zn (90)	D (0.5)	6-PA (10)	A	A	43	A	6.4
	62 Zn (90)	E (0.5)	6-PA (10)	A	A	44	A	6.1
	63 Zn (90)	F (0.5)	6-PA (10)	A	A	44	A	6.0
	17 Zn (90)	A (0.5)	6-PA/PP= 5/5 (10)	A	A	43	A	7.9
	27 Zn (90)	C (0.5)	6-PA/PEI= 5/5 (10)	A	A	45	A	6.3
	28 Zn (90)	C (0.5)	12-PA(10)	A	A	35	A	6.6
	29 Zn (90)	C (0.5)	PS (10)	A	A	42	A	6.1

5 10 15 20 25 30 35 40 50 55

Table 1 (Part 3)

Filler (parts by weight)	Water repellent agent (% by weight)	Matrix polymer (parts by weight)	Rust after		Moldability	Izod impact test kg/cm <sup>2</sup>	Elec- tric resist- ance, mega- ohm
			100 hours	300 hours			
30 Zn (90)	C (0.5)	PC (10)	A	A	44	A	11.9
31 Zn (90)	C (0.5)	PVC (10)	A	A	37	A	9.7
32 Zn (90)	C (0.5)	PMMA (10)	A	A	33	A	5.9
33 Zn (90)	C (0.5)	PPO (10)	A	A	44	A	6.3
34 Zn (90)	C (0.5)	PSO (10)	A	A	51	A	7.1
35 Zn (90)	C (0.5)	PI (10)	A	A	51	A	7.4
36 Zn (90)	C (0.5)	PPS (10)	A	A	53	A	6.2
37 Zn (90)	C (0.5)	SBR (10)	A	A	37	A	17.1
38 Zn (90)	C (0.5)	EPR (10)	A	A	32	A	14.9
39 Zn (90)	C (0.5)	SR (10)	A	A	40	A	13.7
40 Zn (90)	C (0.5)	EVA (10)	A	A	35	A	15.2
41 Zn (90)	C (0.5)	PEE (10)	A	A	39	A	11.7
42 Zn (90)	C (0.5)	POE (10)	A	A	36	A	14.2
64 Zn (90)	G (0.5)	6-PA (10)	A	A	39	A	6.3
65 Zn (90)	H (0.5)	6-PA (10)	A	A	38	A	6.5

Table 1 (Part 4)

Filler (parts by weight)	Water repellent agent (% by weight)	Matrix polymer (parts by weight)	Rust after		Moldability	Izod impact test		Elec- tric resist- ance, mega- ohm
			100 hours	300 hours		Min- imum pres- sure, kg/cm <sup>2</sup>	Ap- pear- ance	
45 Zn (50)	D (0.5)	66-PA (50)	A	A	34	A	11.5	64
46 Zn (70)	D (0.5)	66-PA (30)	A	A	35	A	9.2	56
47 Zn (90)	D (0.5)	66-PA (10)	A	A	41	A	7.5	49
48 Zn (95)	D (0.5)	66-PA (5)	A	A	47	A	5.9	35
49 Zn (90)	D (1.0)	66-PA (10)	A	A	39	A	7.9	50
50 Zn (90)	D (3.0)	66-PA (10)	A	A	37	A	8.0	51
51 Zn (50)	D (0.5)	12-PA (50)	A	A	30	A	9.7	55
52 Zn (90)	D (0.5)	12-PA (30)	A	A	32	A	8.0	49
53 Zn (90)	D (0.5)	12-PA (10)	A	A	33	A	6.9	44
54 Zn (95)	D (0.5)	12-PA (5)	A	A	39	A	5.0	30
55 Zn (90)	D (1.0)	12-PA (10)	A	A	31	A	7.0	45
56 Zn (90)	D (3.0)	12-PA (10)	A	A	30	A	7.1	45
16 Zn (90)	D (3.0)	12-PA (10)	A	A	34	A	6.7	42
26 Zn (90)	C (0.5)	66-PA (10)	A	A	41	A	7.5	50
57 Zn (90)	D (0.5)	66-PA (10)	A	A	35	A	8.9	54

55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 100

Table 1 (Part 5)

Exam- ple	Filler (parts by weight)	Water repellent agent (% by weight)	Matrix polymer (parts by weight)	Rust after		Moldability	Izod impact test kg/cm <sup>2</sup>	Elec- tric resist- ance, mega- ohm
				100 hours	300 hours			
58	Zn (90)	D (0.5)	66-PA (10)	A	A	37	A	7.0
43	Zn (90)	C (0.5)	6PA/PP=5/5(10)	A	A	42	A	8.1
59	Zn (90)	D (0.5)	6-PA/PP=5/5(10)	A	A	40	A	8.2
60	Zn (70)	D (0.5)	6-PA/PP=5/5(30)	A	A	33	A	8.9
61	Zn (50)	D (0.5)	6-PA/PP=5/5(50)	A	A	30	A	10.5
1	Zn (90)	A (0.005)	6-PA (10)	C	D	51	C	4.3
2	Zn (90)	A (6.0)	6-PA (10)	A	A	35	C	6.1
3	Zn (90)	C (0.005)	6-PA (10)	C	D	67	B	4.7
4	Zn (90)	C (6.0)	6-PA (10)	A	A	35	C	6.0
5	Zn (25)	A (0.3)	6-PA (75)	A	A	28	A	13.1
6	Zn (99)	A (0.3)	6-PA (1)	B	C	61	C	1.9

Examples 66 to 103 and Comparative Examples 7 to 13.

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The experimental procedure in each of these Examples and Comparative Examples was substantially the same as in Example 1. Table 2 below shows the formulation of the molding compositions and the results of evaluation undertaken in the same manner as in Example 1.

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Examples 104 to 107 and Comparative Examples 14 and 15.

A molding resin composition was prepared by first blending, in a Henschel mixer of 20 liter capacity, 15 parts by weight of a 6-PA resin, 85 parts by weight of a ZnO powder having a varied average particle 15 diameter shown in Table 3 below, 0.5 part by weight of a low-molecular oxidized polypropylene having an average molecular weight of 3500 and 0.3 part by weight of an aminosilane-based coupling agent and then kneading the blend thoroughly at 220 to 350 °C in a double-screw kneading machine (Model NAS-50, manufactured by Nakatani Machinery Co.).

The thus prepared molding resin compositions were each shaped by injection molding into test plates 20 at 220 to 350 °C using the same injection molding machine as used in Example 1. The molding compositions were evaluated by measuring the minimum molding pressure in the injection molding of the composition and the mechanical and electrical properties of the test plates in the following manner. The results are shown in Table 3.

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Table 2 (Part 1)

Example	Filler (parts by weight)	Water repellent agent (% by weight)	Matrix polymer (parts by weight)	Rust after		Moldability	Izod impact test	Elec- tric resist- ance, mega- ohm
				100 hours	300 hours			
66	ZnO (90)	C (0.5)	6-PA (10)	A	A	43	A	7.1
71	ZnO (90)	A (0.5)	6-PA (10)	A	A	41	A	7.0
84	Cu (90)	C (0.5)	6-PA (10)	A	A	47	A	8.7
85	Cu (90)	A (0.5)	6-PA (10)	A	A	45	A	8.9
86	Fe (90)	C (0.5)	6-PA (10)	A	A	48	A	6.1
87	Fe (90)	A (0.5)	6-PA (10)	A	A	44	A	6.3
88	Fe <sub>2</sub> O <sub>3</sub> (90)	C (0.5)	6-PA (10)	A	A	49	A	5.7
89	Fe <sub>2</sub> O <sub>3</sub> (90)	A (0.5)	6-PA (10)	A	A	44	A	5.9
90	Zn/Fe <sub>2</sub> O <sub>3</sub> =45/45 (90)	A (0.5)	6-PA (10)	A	A	44	A	6.0
91	Zn/ZnO =70/20 (90)	C (0.5)	6-PA (10)	A	A	40	A	7.2
92	N1 (90)	C (0.5)	6-PA (10)	A	A	43	A	6.4
93	Pb (90)	C (0.5)	6-PA (10)	A	A	42	A	7.9
94	Ag (90)	C (0.5)	6-PA (10)	A	A	39	A	8.2
95	Sn (90)	C (0.5)	6-PA (10)	A	A	44	A	7.1

Table 2 (Part 2)

	Filler (parts by weight)	Water repellent agent (% by weight)	Matrix polymer (parts by weight)	Rust after		Moldability	Izod impact test kg/cm <sup>2</sup>	Elec- tric resist- ance, mega- ohm
				100 hours	300 hours			
96	SnO <sub>2</sub> (90)	C (0.5)	6-PA (10)	A	A	4.6	A	6.0
97	SnO <sub>2</sub> (90)	C (0.5)	6-PA (10)	A	A	3.9	A	6.4
98	SnO <sub>2</sub> (90)	C (0.5)	6-PA (10)	A	A	3.7	A	7.2
99	SnO <sub>2</sub> (90)	C (0.5)	6-PA (10)	A	A	3.8	A	6.6
100	SnO <sub>2</sub> (90)	C (0.5)	6-PA (10)	A	A	5.2	A	5.4
101	SnO <sub>2</sub> (90)	C (0.5)	6-PA (10)	A	A	5.1	A	5.9
102	SnO <sub>2</sub> (90)	C (0.5)	6-PA (10)	A	A	4.2	A	6.7
103	SnO <sub>2</sub> (90)	C (0.5)	6-PA (10)	A	A	4.7	A	6.9
7	Fe <sub>2</sub> O <sub>3</sub> (90)	C (0.005)	6-PA (10)	C	D	6.9	C	1.7
8	Fe <sub>2</sub> O <sub>3</sub> (90)	A (0.005)	6-PA (10)	C	D	7.1	C	2.3
9	Zn (90)	A (0.5)	6-PA (10)	B	C	5.9	B	4.3
10	Zn (90)	C (0.5)	6-PA (10)	A	B	6.2	B	3.1
11	Zn (90)	G (0.5)	6-PA (10)	C	D	5.7	B	3.2
12	Fe <sub>2</sub> O <sub>3</sub> (90)	A (0.5)	6-PA (10)	B	C	6.1	B	2.0
13	Fe (90)	C (0.5)	6-PA (10)	B	B	6.4	B	2.3

(1) Molding pressure: a box having dimensions of 90 mm by 150 mm by 70 mm with a wall thickness of 5 mm and a pin gate of 1 mm diameter was shaped by injection molding under the above mentioned conditions to determine the minimum pressure for impregnation in kg/cm<sup>2</sup>G.

5 (2) Mechanical properties: tensile strength in kg/cm<sup>2</sup> of the test plates was determined according to ASTM D-638 and flexural strength and elastic modulus by bending each in kg/cm<sup>2</sup> were determined according to ASTM D-790.

(3) Electrical properties: specific resistance in ohm-cm was determined according to Japan Rubber Association Standard SRJS-2301-1969.

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Table 3

	Average particle diameter of ZnO, $\mu\text{m}$	Molding pressure, $\text{kg}/\text{cm}^2\text{G}$	Tensile strength, $\text{kg}/\text{cm}^2$	Flexural strength, $\text{kg}/\text{cm}^2$	Elastic modulus by bending, $\times 10^4 \text{ kg}/\text{cm}^2$	Specific resistance, $\text{ohm}\cdot\text{cm}$
Example	104	0.3	75	860	1510	12.8
	105	1	70	810	1450	12.5
	106	3	67	795	1320	11.7
	107	5	65	710	1250	10.9
						$1 \times 10^5$
Comparative Example	14	0.1	97	905	1570	13.1
	15	9	60	650	990	$1 \times 10^5$
						$1 \times 10^5$

\* large variation in the values of specific resistance

In these Examples and Comparative Examples, the low-molecular oxidized polypropylene was a commercial product (Biscol TS-200, a product by Sanyo Kasei Co.) and the aminosilane-based coupling agent was aminopropyl triethoxy silane.

Examples 108 to 110 and Comparative Examples 16 and 17.

The formulation and experimental procedure in each of these Examples and Comparative Examples were substantially the same as in Examples 104 to 107 except that the amounts of the 6-PA resin and ZnO, having an average particle diameter of 2  $\mu\text{m}$ , were varied as shown in Table 4 below, which also shows the results of evaluation of the molding resin compositions carried out in the same manner as in the preceding examples.

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Table 4

	6-PA, parts by weight	ZnO, parts by weight	Molding pressure, kg/cm <sup>2</sup> G	Tensile strength, kg/cm <sup>2</sup>	Flexural strength, kg/cm <sup>2</sup>	Elastic modulus by bending, x 10 <sup>4</sup> kg/cm <sup>2</sup>	Specific resistance, ohm·cm
Example	108	40	60	61	870	1550	9.2
	109	20	80	68	875	1470	12.1
	110	5	95	74	760	1350	13.5
Compar- ative Example	16	60	40	49	920	1660	7.4
	17	3	97	150	620	1290	14.6
							1 x 10 <sup>4</sup>

Examples 111 to 113 and Comparative Examples 18 and 19.

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The formulation and experimental procedure were substantially the same as in the preceding examples except that the amounts of the 6-PA resin and ZnO filler were 15 parts by weight and 85 parts by weight, respectively, in each of these Examples and Comparative Examples and the amount of the low-molecular 10 below, which also shows the results of evaluation of the molding resin compositions carried out in the same manner as in the preceding examples.

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Table 5

	Component (C), parts by weight	Molding pressure, kg/cm <sup>2</sup> G	Tensile strength, kg/cm <sup>2</sup>	Flexural strength, kg/cm <sup>2</sup>	Elastic modulus by bending, x 10 <sup>4</sup> kg/cm <sup>2</sup>	Specific resistance, ohm·cm
Example	111	0.1	90	705	1120	10.1
	112	0.7	67	830	1490	12.7
	113	1.5	59	755	1300	11.6
Compar- ative Example	18	0.05	120	520	950	9.7
	19	2.5	51	670	970	9.6

Examples 114 to 117.

The formulation and experimental procedure in each of these Examples were substantially the same as in the preceding examples except that the amount of the component (C) was always 0.5 part by weight and, 5 instead, the average molecular weight thereof was varied as indicated in Table 6 given below, which also shows the results of evaluation of the molding resin compositions carried out in the same manner as in the preceding examples.

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Table 6

	Average molecular weight of component (C)	Molding pressure, g/cm <sup>2</sup> G	Tensile strength, kg/cm <sup>2</sup>	Flexural strength, kg/cm <sup>2</sup>	Elastic modulus by bending, x 10 <sup>4</sup> kg/cm <sup>2</sup>	Specific resistance, ohm·cm
	114	7000	75	815	1460	12.7
	115	15000	72	820	1470	12.9
Example	116	20000	80	830	1500	13.1
	117	25000	90	845	1510	13.4
						1 x 10 <sup>6</sup>

Examples 118 to 120 and Comparative Examples 20 and 21.

The formulation and experimental procedure in each of these Examples and Comparative Examples were substantially the same as in the preceding examples except that the low-molecular oxidized 5 polypropylene as the component (C) always had an average molecular weight of 3500 and the amount of the 3-aminopropyl triethoxy silane as the aminosilane-based coupling agent was varied as indicated in Table 7 below, which also shows the results of evaluation of the molding resin compositions carried out in the same manner as in the preceding examples.

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Table 7

	Aminosi-lane, parts by weight	Molding pressure, kg/cm <sup>2</sup> G	Tensile strength, kg/cm <sup>2</sup>	Flexural strength, kg/cm <sup>2</sup>	Elastic modulus by bending, x 10 <sup>4</sup> kg/cm <sup>2</sup>	Specific resistance, ohm·cm
118	0.1	87	760	1310	11.9	1 x 10 <sup>5</sup>
119	0.7	65	830	1490	13.0	1 x 10 <sup>5</sup>
120	1.5	61	760	1310	12.1	1 x 10 <sup>5</sup>
Comparative Example 20	0.05	105	550	970	10.1	1 x 10 <sup>7</sup>
Comparative Example 21	2.5	57	720	960	10.5	1 x 10 <sup>8</sup> *

\* large variation in the values as measured

Examples 121 to 134.

The formulation and experimental procedure in each of these Examples were substantially the same as in the preceding Examples except that the amount of the 3-aminopropyl triethoxy silane was always 0.3 part by weight and the thermoplastic resin, taken in an amount of 15 parts by weight, was not the 6-PA resin but one of the polymers or a combination of two polymers in a proportion as indicated in Table 8 below, which also shows the results of evaluation of the molding compositions carried out in the same manner as in the preceding examples. The values of specific resistance of the test plates were each  $1 \times 10^5$  ohm•cm.

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Table 8

Example	Polymer(s) (ratio by weight)	Molding pressure, kg/cm <sup>2</sup> G	Tensile strength, kg/cm <sup>2</sup>	Flexural strength, kg/cm <sup>2</sup>	Elastic modulus by bending, x 10 <sup>4</sup> kg/cm <sup>2</sup>
121	66-PA	73	820	1470	12.9
122	MXDA	75	840	1500	13.0
123	PET	73	890	1620	13.4
124	PBT	74	795	1240	11.1
125	PPO	77	810	1450	12.7
126	PC	76	835	1490	12.9
127	ABS	67	720	1150	10.1
128	POM	70	805	1390	12.0
129	PP	47	510	910	6.2
130	PE	44	460	810	5.4
131	PPO/6-PA (9:6)	74	830	1490	12.9
132	PC/PET (10:5)	74	870	1520	12.9
133	PBT/PET (9:6)	74	850	1430	12.7
134	PSO	85	810	1350	13.1

Examples 135 to 139.

The formulation and experimental procedure in each of these Examples were substantially the same as in the preceding Examples except that the polymer for the matrix was one of those indicated in Table 9 below and 0.3 part by weight of 3-aminopropyl triethoxy silane was replaced with 0.5 part by weight of a dimethyl silicone fluid. Table 9 below also shows the results of evaluation of the molding resin compositions carried out in the same manner as in the preceding examples. The values of specific resistance of the test plates were each  $1 \times 10^5$  ohm•cm.

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Table 9

Example	Polymer	Molding pressure, kg/cm <sup>2</sup>	Tensile strength, kg/cm <sup>2</sup>	Flexural strength, kg/cm <sup>2</sup>	Elastic modulus by bending, $\times 10^4$ kg/cm <sup>2</sup>
135	6-PA	65	795	1390	12.3
136	12-PA	61	720	1190	11.7
137	66-PA	71	835	1510	13.1
138	PBT	71	815	1290	11.9
139	PP	44	525	990	6.4

Examples 140 to 144.

The formulation and experimental procedure in each of these Examples were substantially the same as in the preceding Examples except that the polymer for the matrix phase was one of those indicated in Table 5 10 below and the dimethyl silicone fluid was replaced with the same amount of isopropyl triisostearoyl titanate as a titanate-based coupling agent. Table 10 below also shows the results of evaluation of the 10 molding resin compositions carried out in the same manner as in the preceding examples. The values of specific resistance of the test plates were each  $1 \times 10^5$  ohm•cm.

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Table 10

Example	Polymer	Molding pressure, kg/cm <sup>2</sup>	Tensile strength, kg/cm <sup>2</sup>	Flexural strength, kg/cm <sup>2</sup>	Elastic modulus by bending, $\times 10^4$ kg/cm <sup>2</sup>
140	6-PA	71	805	1410	12.9
141	12-PA	66	700	1190	10.1
142	66-PA	72	840	1530	13.3
143	PBT	73	815	1280	12.0
144	PP	46	510	975	6.1

## Preparation Example 1 (Preparation of modified polypropylene)

5 Into a three-necked flask equipped with a stirrer, thermometer and reflux condenser and having a separable cover were introduced 100 parts by weight of a polypropylene resin having a density of 0.91 g/cm<sup>3</sup> and a melt index MI of 8 g/10 minutes (J700G, a product by Idemitsu Petrochemical Co.), 5 parts by weight of a 1,4-polybutadiene having a number-average molecular weight of 3000 and terminated at each 10 molecular chain end with a hydroxy group (Poly bd R45HT, a product by ARCO Chem. Div.), 20 parts by weight of maleic anhydride, 1.72 parts by weight of dicumyl peroxide and 600 parts by weight of xylene and the mixture was heated under agitation at 120 °C for 1 hour and then at 140 °C for 3 hours to effect the reaction.

15 After completion of the reaction, the reaction mixture was poured into a large volume of acetone and the precipitates formed in acetone were collected by filtration with suction and dried at 70 °C for 50 hours to give a white powder. This powder was subjected to extraction with acetone in a Soxhlet extractor for 16 hours to give a modified polypropylene as the product by removing unreacted polybutadiene and maleic anhydride.

## Examples 145 to 172 and Comparative Examples 22 to 29.

20 A Henschel mixer was charged with 10 parts by weight of one of the fibrous fillers indicated in Table 11, 70 parts by weight of a zinc powder having an average particle diameter of about 3 μm and 0.5 part by weight of a dimethyl silicone fluid and operated at a velocity of 1000 rpm for 5 minutes at a temperature of 60 to 100 °C to coat the surface of the fibers and zinc particles with the silicone fluid. Thereafter, 20 parts by weight of a 6-PA resin were introduced into the mixer and thoroughly blended together. The thus 25 obtained blend was further kneaded at 220 to 350 °C in a double-screw extruder machine to give a molding resin composition which was then shaped into test plates at 220 to 350 °C by injection molding using the same injection machine as used in Example 1. The molding resin compositions were evaluated for the moldability of the composition, mechanical properties of the test plates, molding shrinkage of the molded articles and warping distortion of the molded articles in the following manner.

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## (1) Moldability of the molding composition

35 A box having dimensions of 90 mm by 150 mm by 70 mm with a wall thickness of 5 mm and a pin gate of 1 mm diameter was shaped from the molding composition by injection molding using an injection molding machine (Model IS-125, manufactured by Toshiba Machines Co.) operated under the standard conditions of a cylinder temperature of 220 to 300 °C, temperature of metal mold of 75 to 100 °C, injection pressure of 60 kg/cm<sup>2</sup> and shot time of 20 seconds and the moldability of the molding composition was 40 evaluated according to the following criteria in three ratings in terms of the reproducibility of the box configuration by the injection molding and the injection pressure.

A: quite satisfactory

B: appearance of sink marks at some portions, somewhat higher injection pressure than the standard pressure

C: partly incomplete box configuration, injection pressure of 100 kg/cm<sup>2</sup>G or higher

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## (2) Mechanical properties of the test plates

50 Tensile strength was determined according to ASTM D-638, Izod impact value was determined according to ASTM D-256 and flexural strength and elastic modulus by bending were determined according to ASTM D-790.

## (3) Molding shrinkage of molded articles

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Square test plates of 76 mm by 76 mm wide and 3.2 mm thick were shaped from the molding composition by injection molding under a sufficiently high injection pressure and the changes of the dimensions in % were determined in the molding direction (MD) and transverse direction (TD).

## (4) Warping distortion of shaped articles

5 A circular disc of 45 mm diameter and 2 mm thickness was shaped by injection molding under the same conditions as above and warping of the disc was evaluated by the height  $\alpha$  of the highest point when the disc was placed on a horizontal plane. The results were given in three ratings of A, B and C according to the following criteria.

A:  $\alpha < 0.5$  mm

B:  $0.5$  mm  $\leq \alpha \leq 1$  mm

C:  $\alpha > 1$  mm

10 Table 11 given below shows the formulation of the molding resin compositions and the results of the evaluation thereof performed in the above described manner. In Table 11, the kinds of the fibrous fillers are indicated with the symbols of GF, SF, BF, PT, CF, SCF and APAF for glass fibers, stainless steel fibers, brass fibers, whiskers of potassium titanate, carbon fibers, silicon carbide fibers and aromatic polyamide fibers, respectively.

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Table 11 (Part 1)

		Fibrous filler			Tensile strength, kg/cm <sup>2</sup>	Izod impact value, kg·cm/cm	Flexural strength, kg/cm <sup>2</sup>
	Kind	Length, mm	Diameter, μm	Aspect ratio			
Example	145	10	4	2500	1650	101	2450
	146	10	13	770	1550	94	2300
	147	6	4	1500	1600	97	2350
	148	6	13	462	1570	94	2250
	149	3	4	750	1530	94	2280
	150	3	12	231	1500	94	2200
	151	1	4	250	1500	90	2150
	152	1	13	77	1350	80	2050
	153	10	30	333	1450	77	1900
	154	10	60	167	1300	73	1810
SF	155	6	30	200	1330	73	1800
	156	6	60	100	1200	66	1760
	157	3	30	100	1200	65	1720
	158	3	60	50	1150	60	1670
	159	10	30	333	1430	75	1900
	160	10	60	167	1290	71	1820
	161	6	30	200	1300	71	1790
	162	6	60	100	1210	66	1720
	163	3	30	100	1190	64	1710
	164	3	60	50	1110	61	1650

Table 11 (Part 2)

	Elastic modulus by bending, x 10 <sup>4</sup> kg/cm <sup>2</sup>	Molding shrinkage, M D      T D		Warping distortion	Moldability	Density, g/cm <sup>3</sup>
		M D	T D			
145	12.7	0.82	0.45	B	B	3.21
146	12.2	0.80	0.45	A	A	3.21
147	12.0	0.79	0.45	A	A	3.21
148	12.1	0.80	0.45	A	A	3.21
149	12.1	0.80	0.45	A	A	3.21
150	11.5	0.82	0.52	A	A	3.21
151	10.9	0.82	0.51	A	A	3.21
152	10.1	0.85	0.60	A	A	3.21
153	12.5	0.91	0.55	A	A	3.49
154	12.0	0.89	0.54	A	A	3.49
155	11.9	0.86	0.54	A	A	3.49
156	11.6	0.85	0.58	A	A	3.49
157	11.6	0.85	0.57	A	A	3.49
158	11.3	0.85	0.61	A	A	3.49
159	12.7	0.92	0.57	A	A	3.50
160	11.9	0.90	0.55	A	A	3.50
161	11.9	0.87	0.54	A	A	3.50
162	11.4	0.86	0.56	A	A	3.50
163	11.4	0.85	0.58	A	A	3.50
164	11.1	0.85	0.63	A	A	3.50

Table 11 (Part 3)

		Fibrous filler			Tensile strength, kg/cm <sup>2</sup>	Izod impact value, kg·cm/cm	Flexural strength, kg/cm <sup>2</sup>
Kind	Length, mm	Diameter, μm	Aspect ratio				
Example	165	PT	0.01	0.1	100	1250	100
	166		0.02	0.1	200	1310	105
	167	CF	10	10	1000	1820	109
	168		3	10	300	1650	102
	169	SCF	10	10	1000	2030	111
	170		3	10	300	1910	104
	171	APAF	6	12	500	1850	109
	172		3	12	250	1710	104
	22	GF	12	4	3000	1710	105
	23		0.12	4	30	820	51
Comparative	24	SF	30	10	3000	1500	79
	25		0.3	10	30	710	47
	26	BF	30	10	3000	1410	71
	27		0.3	10	30	660	40
	28	CF	30	10	3000	1900	110
	29		0.3	10	30	790	59
							1110

Table 11 (Part 4)

	Elastic modulus by bending, x 10 <sup>4</sup> kg/cm <sup>2</sup>	Molding shrinkage, %			Warping distortion	Moldability	Density, g/cm <sup>3</sup>
		M	D	T D			
Example	165	10.0	0.75	0.44	A	A	3.30
	166	10.5	0.75	0.45	A	A	3.30
	167	9.7	0.80	0.45	A	A	2.97
	168	8.1	0.80	0.45	A	A	2.97
	169	15.4	0.78	0.42	A	A	3.28
	170	14.2	0.80	0.44	A	A	3.28
	171	10.9	0.80	0.45	A	A	2.92
	172	9.2	0.80	0.45	A	A	2.92
	22	12.9	0.90	0.45	C	B	3.21
	23	7.7	0.79	0.57	A	A	3.21
Comparative Example	24	12.7	0.93	0.55	C	B	3.49
	25	7.1	0.81	0.59	A	A	3.49
	26	12.4	0.93	0.55	C	B	3.50
	27	6.9	0.82	0.59	A	A	3.50
	28	10.6	0.89	0.43	C	B	2.97
	29	8.2	0.75	0.42	A	A	2.97

Examples 173 to 183 and Comparative Examples 30 to 39.

The experimental procedure in each of these Examples and Comparative Examples was substantially the same as in the preceding examples except that each of the molding resin compositions was compounded from 20 parts by weight of the 6-PA resin, a varied amount as indicated in Table 12 below of a zinc powder having an average particle diameter of about 3  $\mu$ m and a varied amount of a fibrous filler, i.e. glass fibers (GF), stainless steel fibers (SF), potassium titanate whiskers (PT) or carbon fibers (CF), as indicated in Table 12. The results of the evaluation of these molding resin compositions are also shown in Table 12 for the same items as in Table 11 in the preceding examples.

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Table 12 (Part 1)

	Zinc powder, parts by weight	Fibrous filler			Tensile strength, kg/cm <sup>2</sup>	Izod impact value, kg·cm/cm	Flexural strength, kg/cm <sup>2</sup>
		Kind	Aspect ratio	Parts by weight			
Example	173 75			750 5	1270	80	1770
	174 50	GF	750	30	1890	110	2670
	175 75		231	5	1210	80	1690
	176 50		231	30	1820	97	2570
	177 75	SF	200	5	1110	69	1520
	178 50		200	30	1690	87	2050
Comparative Example	179 75	PT	200	5	1190	90	1620
	180 50		200	30	1590	118	2300
	181 75		300	5	1400	91	1690
	182 50	CF	300	30	1870	105	2010
	183 30		300	40	1990	111	2220
	30 79		750	1	870	59	1260
	31 20	GF	750	60	2110	115	2790
	32 79		231	1	800	57	1200
	33 20		231	60	2050	111	2550
	34 79	SF	200	1	810	47	1020
	35 20		200	60	1820	89	2560
	36 79	PT	200	1	770	79	1090
	37 20		200	60	1780	121	2520
	38 79	CF	300	1	900	79	1110
	39 20		300	60	2110	114	2300

T a b l e 12 (Part 2)

	Elastic modulus by bending, $\times 10^4$ kg/cm <sup>2</sup>	Molding shrinkage, %	Warping distortion	Moldability	Density, g/cm <sup>3</sup>
		M D	T D		
Example	173	10.9	0.85	0.50	A
	174	13.2	0.75	0.44	A
	175	10.1	0.85	0.51	A
	176	12.7	0.74	0.43	A
	177	10.0	0.88	0.55	A
	178	12.1	0.79	0.50	A
	179	8.9	0.79	0.47	A
	180	12.2	0.71	0.41	A
	181	7.2	0.83	0.46	A
	182	10.9	0.77	0.44	A
	183	11.7	0.76	0.44	A
	30	8.2	1.00	0.81	C
	31	15.4	0.70	0.41	A
	32	7.9	1.01	0.83	C
	33	14.0	0.73	0.42	A
	34	7.9	1.00	0.82	C
Comparative Example	35	13.7	0.75	0.47	A
	36	7.1	1.00	0.79	C
	37	13.9	0.70	0.40	A
	38	6.2	1.01	0.80	C
	39	12.8	0.75	0.43	A

### Examples 184 to 204 and Comparative Examples 40 to 45

The experimental procedure in each of these Examples and Comparative Examples was substantially the same as in the preceding examples except that the molding resin compositions were each compounded from 20 parts by weight of the 6-PA resin, 10 parts by weight of glass fibers having an aspect ratio of 231 and 70 parts by weight of a particulate filler indicated in Table 13 below, which also shows the results of the evaluation of the molding compositions.

Examples 205 to 223.

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The experimental procedure in each of these Examples was substantially the same as in Examples 145 to 172 except that the molding resin compositions were each compounded from 10 parts by weight of glass fibers having an aspect ratio of 231, 70 parts by weight of zinc powder having an average particle diameter of about 3  $\mu\text{m}$  and 20 parts by weight of one kind or a combination of two kinds of the thermoplastic resins indicated in Table 14 below, which also shows the results of the evaluation of the molding compositions. When two kinds of the thermoplastic resins were used, they were taken in equal amounts.

Table 13

	Particulate filler		Warping distortion	Moldability	Density, g/cm <sup>3</sup>
	Kind	Average particle diameter, $\mu\text{m}$			
184	Zinc	0.5	105	A	3.21
185		10	82	A	3.21
186		0.5	113	A	2.86
187	Zinc oxide	3	97	A	2.86
188		10	76	A	2.86
189		0.7	101	A	3.32
190	Iron	3	89	A	3.32
191		10	80	A	3.32
192		0.5	100	A	2.86
193	Ferrite	3	89	A	2.86
194		10	81	A	2.86
195	Stainless steel	0.5	96	A	3.32
196		3	84	A	3.32
197		10	77	A	3.32
198		0.5	97	A	3.39
199	Brass	3	84	A	3.39
200		10	78	A	3.39
201	Lead	5	89	A	3.65
202	Solder alloy	5	92	A	3.37
203	Copper	5	86	A	3.45
204	Nickel	5	86	A	3.44
40	Zinc oxide	0.1	113	C	2.94
41		25	60	C	2.94
42	Iron	0.1	109	A	3.32
43		30	61	C	3.32
44	Ferrite	0.1	105	A	2.86
45		30	62	C	2.86

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Table 14

Exam- ple No.	Resins	Tensile strength, kg/cm <sup>2</sup>	Izod impact strength, kg·cm/cm	Flexural Strength, kg/cm <sup>2</sup>	Elasti- modulus by bend- ing, kg/cm <sup>2</sup> x 10 <sup>4</sup>	Molding shrinkage, %		Warp- ing distor- tion	Molda- bility	Den- sity, g/cm <sup>3</sup>
						MD	TD			
205	66-PA	1590	80	2300	12.1	0.80	0.50	A	A	3.21
206	MXDA	1580	93	2250	12.9	0.71	0.42	A	A	3.21
207	PBT	1200	85	1750	11.1	0.70	0.41	A	A	3.47
208	PET	1620	90	1800	11.2	0.70	0.42	A	A	3.33
209	PC	1490	155	1910	10.9	0.75	0.45	A	A	3.31
210	POM	1410	95	1900	11.9	0.82	0.51	A	A	3.60
211	ABS	1020	110	1500	9.9	0.72	0.44	A	A	3.07
212	PP	690	65	850	5.7	0.89	0.62	A	A	2.80
213	PE	620	50	790	4.9	0.91	0.67	A	A	2.91
214	PVC	650	31	970	10.1	0.85	0.50	A	A	3.52
215	PMMA	710	30	1520	12.9	0.86	0.52	A	A	3.30
216	PI	1280	95	2310	13.9	0.69	0.39	A	A	3.63
217	PSO	1370	92	2010	12.1	0.85	0.55	A	A	3.37
218	PPO	1490	115	1870	10.2	0.77	0.46	A	A	3.08
219	6-PA/PET	1600	88	2050	11.2	0.77	0.48	A	A	3.28
220	6-PA/PPO	1510	97	2000	11.0	0.80	0.49	A	A	3.15
221	6-PA/PBT	1350	87	1970	11.2	0.75	0.45	A	A	3.20
222	PC/PET	1590	111	1860	11.1	0.73	0.43	A	A	3.34
223	PPS	1510	87	2700	21.7	0.51	0.33	A	A	3.83

### Examples 224 to 243.

The experimental procedure in each of these Examples was substantially the same as in Examples 145 to 172 except that the molding compositions were each compounded from 10 parts by weight of glass fibers having an aspect ratio of 231 as a fibrous filler, a varied amount indicated in Table 15 below of a powder of zinc (Examples 224 to 233) or zinc oxide (Examples 234 to 243) each having an average particle diameter of about 3  $\mu\text{m}$  as a particulate filler and a varied amount of a thermoplastic resin indicated in Table 15, which also shows the results of the evaluation of the molding compositions.

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Table 15

Particu- late filler, Kind parts by weight	Resin	Tensile strength, kg/cm <sup>2</sup>	Izod impact strength, kg.cm/cm <sup>2</sup>	Flex- ural strength, kg/cm <sup>2</sup>	Elastic modulus by bending x 10 <sup>4</sup> kg/cm <sup>2</sup>	Molding shrinkage, %		Warp- ing distor- tion	Molda- bility	Den- sity, g/cm <sup>3</sup>
						MD	TD			
224	85	6-PA	5	1110	77	1750	13.9	0.70	0.41	A 4.99
225	60	6-PA	30	1650	95	2350	10.3	0.85	0.53	A 3.80
226	85	PBT	5	850	67	1250	13.1	0.66	0.37	A 5.13
227	60	PBT	30	1350	95	1900	9.1	0.75	0.45	A 2.85
228	85	PET	5	1210	69	1360	13.2	0.67	0.37	A 5.05
229	60	PET	30	1790	99	1950	9.2	0.76	0.45	A 2.71
230	85	PP0	5	1100	90	1370	12.2	0.72	0.44	A 4.90
231	60	PP0	30	1640	118	2030	8.2	0.81	0.52	A 3.53
232	85	PC	5	1090	110	1410	12.9	0.67	0.38	A 5.05
233	60	PC	30	1650	165	2060	8.9	0.79	0.48	A 2.71
234	85	6-PA	5	1330	97	1930	15.4	0.69	0.40	A 4.04
235	60	6-PA	30	1830	115	2550	11.7	0.83	0.52	A 2.40
236	85	PBT	5	1050	87	1440	14.6	0.66	0.36	A 4.13
237	60	PBT	30	1550	115	2090	10.5	0.74	0.45	A 2.60
238	85	PET	5	1400	89	1510	14.6	0.66	0.57	A 4.08
239	60	PET	30	1950	119	2140	10.6	0.75	0.43	A 2.50
240	85	PP0	5	1290	110	1570	13.6	0.70	0.42	A 3.99
241	60	PP0	30	1870	138	2220	9.7	0.80	0.51	A 2.28
242	85	PC	5	1290	130	1630	13.4	0.65	0.37	A 4.08
243	60	PC	30	1830	190	2230	10.3	0.77	0.46	A 4.08

Examples 244 to 251.

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The experimental procedure in each of these Examples was substantially the same as in Examples 145 to 172 except that the molding resin compositions were each compounded from 10 parts by weight of glass fibers having an aspect ratio of 231, 70 parts by weight of a zinc powder having an average particle diameter of about 3  $\mu\text{m}$  and 20 parts by weight of a thermoplastic resin indicated in Table 16 below without or with further admixture of 2 parts by weight of the modified polypropylene resin prepared in Preparation Example 1 as a modifier. The fibrous and particulate fillers were used after a surface treatment with 0.5 part by weight of a dimethyl silicone fluid as the water repellent agent. Table 16 below also shows the results of the evaluation of the molding compositions.

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Table 16

Example No.	Resin	Modifier	Izod impact strength, kg.cm/cm	Warping distortion	Moldability	Density, g/cm <sup>3</sup>
244	6-PA	Yes	106	A	A	3.20
245	PBT	Yes	98	A	A	3.46
246	PET	Yes	103	A	A	3.31
247	PPO	Yes	122	A	A	3.06
248	PC	Yes	175	A	A	3.30
249	66-PA	No	97	A	A	3.20
250	12-PA	No	87	A	A	3.00
251	PP	No	69	A	A	2.80

Examples 252 to 261.

The experimental procedure in each of these Examples was substantially the same as in Examples 244 to 251 using the thermoplastic resin indicated in Table 17 below excepting replacement of the zinc powder with the same amount of a zinc oxide powder having an average particle diameter of about 3  $\mu\text{m}$ . Table 17 also shows the results of the evaluation of the molding compositions.

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Table 17

Example No.	Resin	Modifier	Izod impact strength, kg.cm/cm	Warping distortion	Moldability	Density, g/cm <sup>3</sup>
252	6-PA	Yes	117	A	A	2.86
253	PET	Yes	122	A	A	2.94
254	PPO	Yes	137	A	A	2.75
255	PC	Yes	200<	A	A	2.74
256	PET	No	117	A	A	2.94
257	PPO	No	130	A	A	2.75
258	PC	No	200<	A	A	2.74
259	66-PA	No	119	A	A	2.86
260	12-PA	No	98	A	A	2.76
261	PP	No	81	A	A	2.58

## Claims

1. A thermoplastic polymeric molding composition which comprises:
  - (A) from 2 to 70 parts by weight of a thermoplastic polymer as the matrix phase; and
  - (B) from 98 to 30 parts by weight of a metallic filler, of which the particles have a surface coated with a water repellent agent, the amount of the water repellent agent being in the range from 0.01 to 5% by weight based on the metallic filler before coating therewith.
2. The thermoplastic polymeric molding composition as claimed in claim 1 which further comprises:
  - (C) a low-molecular oxidized polypropylene in an amount in the range from 0.1 to 2% by weight based on the total amount of the components (A) and (B).
3. A thermoplastic polymeric molding composition which comprises:
  - (A) from 2 to 70 parts by weight of a thermoplastic polymer as the matrix; and
  - (B) from 98 to 30 parts by weight of a filler which is a combination of
    - (B-1) a metallic particulate filler having an average particle diameter in the range from 0.1 to 20  $\mu\text{m}$ , and
    - (B-2) a fibrous filler having an aspect ratio in the range from 50 to 2500, in a weight ratio of (B-1):(B-2) in the range from 1:1 to 30:1, the surface of the particles of the component (B-1) and the fibers of the component (B-2) being coated with a water repellent agent in an amount in the range from 0.01 to 5% by weight based on the total amount of the components (B-1) and (B-2) before coating therewith.
4. The thermoplastic polymeric molding composition as claimed in claim 3 which further comprises:
  - (C) a low-molecular oxidized polypropylene in an amount in the range from 0.1 to 2% by weight based on the total amount of the components (A) and (B).
5. The thermoplastic polymeric molding composition as claimed in claim 1 wherein the thermoplastic polymer is selected from the group consisting of polyamide resins, polypropylenes and poly(butylene terephthalates).
6. The thermoplastic polymeric molding composition as claimed in claim 3 wherein the thermoplastic polymer is selected from the group consisting of polyamide resins, polypropylenes and poly(butylene terephthalates).
7. The thermoplastic polymeric molding composition as claimed in claim 1 wherein the metallic filler as the component (B) is a powder of metallic zinc.
8. The thermoplastic polymeric molding composition as claimed in claim 3 wherein the metallic particulate filler as the component (B-1) is a powder of metallic zinc.
9. The thermoplastic polymeric molding composition as claimed in claim 1 wherein the metallic filler as the component (B) is a powder of zinc oxide.
10. The thermoplastic polymeric molding composition as claimed in claim 3 wherein the metallic particulate filler as the component (B-1) is a powder of zinc oxide.
11. The thermoplastic polymeric molding composition as claimed in claim 3 wherein the fibrous filler as the component (B-2) is selected from the group consisting of glass fibers, carbon fibers, stainless steel fibers, potassium titanate whiskers and aromatic polyamide fibers.
12. The thermoplastic polymeric molding composition as claimed in claim 1 wherein the water repellent agent is selected from the group consisting of silane coupling agents, titanate coupling agents and silicone fluids.
13. The thermoplastic polymeric molding composition as claimed in claim 3 wherein the water repellent agent is selected from the group consisting of silane coupling agents, titanate coupling agents and silicone fluids.
14. The thermoplastic polymeric molding composition as claimed in claim 1 wherein the water repellent agent is selected from the group consisting of 3-aminopropyl triethoxy silane, N-(2-aminoethyl)-3-aminopropyl trimethoxy silane, isopropyl triisostearoyl titanate, isopropyl tri(N-aminoethyl aminoethyl) titanate, dimethyl silicone fluids and methyl hydrogen polysiloxanes.
15. The thermoplastic polymeric molding composition as claimed in claim 3 wherein the water repellent agent is selected from the group consisting of 3-aminopropyl triethoxy silane, N-(2-aminoethyl)-3-aminopropyl trimethoxy silane, isopropyl triisostearoyl titanate, isopropyl tri(n-amidoethyl aminoethyl) titanate, dimethyl silicone fluids and methyl hydrogen polysiloxanes.
16. The thermoplastic polymeric molding composition as claimed in claim 2 wherein the low-molecular oxidized polypropylene as the component (C) has an average molecular weight in the range from 1500 to 20000.

17. The thermoplastic polymeric molding composition as claimed in claim 4 wherein the low-molecular oxidized polypropylene as the component (C) has an average molecular weight in the range from 1500 to 20000.

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㉓ A thermoplastic resin-based molding composition.

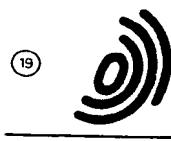
㉔ The thermoplastic polymeric molding composition of the invention has good moldability in shaping by injection molding, extrusion molding and compression molding and capable of giving shaped articles having good machinability in mechanical working such as cutting, grinding and lathing. The composition is compounded from 2 to 70 parts by weight of a thermoplastic polymer such as a polyamide resin and from 98 to 30 parts by weight of a metallic filler such as zinc powder and zinc oxide powder having a surface coated with a water repellent agent

such as silane coupling agents, titanate coupling agents and silicone fluids in a specified amount. A part of the above mentioned particulate filler may optionally be replaced with a fibrous filler such as glass fibers and carbon fibers so that the shaped articles of the molding composition may be imparted with increased impact strength.



EP 87 11 5474

DOCUMENTS CONSIDERED TO BE RELEVANT									
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)						
X	US-A-3 769 260 (L. SEGAL) * Claims; column 4, line 45 - column 5, line 33; column 6, lines 20-30 *	1-6, 11-13	C 08 K 9/04 C 08 K 9/06 C 08 K 3/08 C 08 K 3/22						
P, X	CHEMICAL ABSTRACTS, vol. 107, no. 24, 14th December 1987, page 44, abstract no. 218680w, Columbus, Ohio, US; & JP-A-62 79 259 (SEIKO EPSON CORP.) 11-04-1987 * Abstract *	3, 6, 11, 13, 15							
X	GB-A-2 117 410 (MITSUBISHI PETROCHEMICAL CO. LTD) * Claims *	1, 5, 7, 12, 14							
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TECHNICAL FIELDS SEARCHED (Int. Cl.4)									
C 08 K C 08 L									
<p>The present search report has been drawn up for all claims</p> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 33%;">Place of search</td> <td style="width: 33%;">Date of completion of the search</td> <td style="width: 34%;">Examiner</td> </tr> <tr> <td>THE HAGUE</td> <td>23-10-1989</td> <td>DE LOS ARCOS Y VELAZQUEZ</td> </tr> </table>				Place of search	Date of completion of the search	Examiner	THE HAGUE	23-10-1989	DE LOS ARCOS Y VELAZQUEZ
Place of search	Date of completion of the search	Examiner							
THE HAGUE	23-10-1989	DE LOS ARCOS Y VELAZQUEZ							
CATEGORY OF CITED DOCUMENTS		<p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ..... &amp; : member of the same patent family, corresponding document</p>							
<p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p>									



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(54) **Aluminiumhydroxid für die Einmischung in Kunststoff und Verfahren zu seiner Herstellung.**

(57) Bisher war es nicht möglich, mit gemahlenem Hydroxid mit einer mittleren Korngröße von 10 - 15  $\mu\text{m}$  Füllgrade von mehr als 160 Teilen Hydroxid auf 100 Teile Kunsthärz zu erreichen.

Es soll ein Aluminiumhydroxid zur Flammfestmachung von Kunststoffen und Verfahren zu seiner Herstellung sowie ein flammgeschützter Kunststoff auf Basis von Duroplasten entwickelt werden, wobei das Aluminiumhydroxid mit einem Füllgrad von mehr als 160 Teilen Aluminiumhydroxid auf 100 Teile Kunsthärz einmischbar ist und dabei eine günstige Viskosität aufweist sowie eine glatte Oberfläche an dem daraus hergestellten Fertigteile zeigt. Das gemahlene Aluminiumhydroxid zeichnet sich dadurch aus, daß die Kornobergrenze bei 63  $\mu\text{m}$  mit max. 0,5 % begrenzt ist und daß die Breite B der Kornverteilung, gemessen als  $B = \sqrt{d_{90}} - \sqrt{d_{10}}$ , zwischen 4 - 5 liegt. Das Verfahren zur Herstellung eines Aluminiumhydroxids ist dadurch gekennzeichnet, daß eine Mühle mit Mahlkörpern aus Keramik wie Kugel- oder Trommelmühle, vorzugsweise Schwingmühle, eingesetzt wird.

Das erfindungsgemäße Aluminiumhydroxid wird für die Einmischung in Kunststoffe vom Typ Duroplaste verwendet.

Die Erfindung betrifft ein Aluminiumhydroxid für die Einmischung in Kunststoffe vom Typ Duroplaste, ein Verfahren zur Herstellung des Aluminiumhydroxids durch Mahlung sowie einen flammgeschützten Kunststoff auf Basis von Duroplasten.

5 In der Kunststoffindustrie werden flammhemmende Aluminiumhydroxide mit möglichst hohen Füllgraden eingesetzt. Es war bisher nicht möglich, mit gemahlenem Hydroxid mit einer mittleren Korngröße von 10 - 15  $\mu\text{m}$  Füllgrade von mehr als 160 Teilen Hydroxid auf 100 Teile Kunsthärz zu erreichen.

Bei der Flammfestmachung von Fassadenplatten, elektrischen Bauteilen sowie faserverstärkten Verbundteilen für Automobilindustrie ist es ferner wichtig, daß das Harz bei möglichst hohen Füllgraden an 10 Aluminiumhydroxid noch gut verarbeitbar ist. Dies wird erreicht durch eine möglichst niedrige Viskosität, die jedoch üblicherweise mit dem Füllgrad ansteigt.

Als weiteres wichtiges Kriterium muß die Oberfläche des Fertigteils zumindest an allen sichtbaren Flächen glatt sein. Auch diese Anforderung ist bei hohen Füllgraden an Aluminiumhydroxid schwer zu erfüllen.

15 Aufgabe der vorliegenden Erfindung ist es, ein Aluminiumhydroxid zur Flammfestmachung von Kunststoffen und ein Verfahren zu seiner Herstellung sowie einen flammgeschützten Kunststoff auf Basis von Duroplasten zu entwickeln, wobei das Aluminiumhydroxid mit einem Füllgrad von mehr als 160 Teilen Aluminiumhydroxid auf 100 Teile Kunsthärz einmischbar und dabei eine günstige Viskosität aufweist sowie eine glatte Oberfläche an dem daraus hergestellten Fertigteil zeigt.

20 Die Aufgabe wird durch die in den Patentansprüchen angegebenen Merkmale gelöst. Es hat sich gezeigt, daß die Füllstoffe dann ein besonders gutes Viskositätsverhalten aufweisen, wenn sie sich einer Fullerkurve annähern. Die Fullerkurve ist definiert durch:

$$25 \quad D = \sqrt{\frac{d}{d_{\max}}} \cdot 100 \text{ (%)}$$

mit

30  $D =$  Siebdurchgang (%)  
 $d =$  Korngröße ( $\mu\text{m}$ )  
 $d_{\max} =$  maximale Korngröße ( $\mu\text{m}$ ).

Das erfindungsgemäße Aluminiumhydroxid läßt sich durch die in Tabelle 1 angegebenen Kornverteilungen näher beschreiben. Zum Vergleich wurden handelsübliche Produkte anderer Hersteller herangezogen 35 und mit V1 bis 4 bezeichnet. Zur Verdeutlichung der Unterschiede der Kornverteilungen sind in Tabelle 1 die Parameter  $d_{10}$ ,  $d_{50}$  und  $d_{90}$  sowie Breite  $B = \sqrt{d_{90}} - \sqrt{d_{10}}$  mit den Werten nach Fuller verglichen. Die Fullerkurve beschreibt dabei den Zustand einer Kornverteilung, bei der das Lückenvolumen bei gegebenem Maximalkorn gegen 0 geht (s. Harders-Kienow, Feuerfestkunde, S. 78-82).

40 Bei den in Tabelle 1 aufgelisteten Werten wurde rechnerisch von einer mittleren Korngröße  $d_{50} = 11 \mu\text{m}$  ausgegangen. Die Werte für  $d_{10}$  und  $d_{90}$  wurden graphisch nach dem Siebdurchgang ermittelt (s. Abb. 1). Aus Tabelle 1 geht hervor, daß die Kornverteilung des erfindungsgemäßen Produktes der idealen Fullerkurve in diesem Feinheitsbereich am nächsten kommt.

45 Das Viskositätsverhalten des erfindungsgemäßen Produktes wird in Abb. 2 im Vergleich zu handelsüblichen Hydroxiden V1 bis V4 dargestellt. Aufgetragen ist die relative Viskosität über den Füllgrad in einem ungesättigten Polyesterharz von Typ Leguval N 22, wobei die Meßergebnisse im gefüllten Harz dividiert wurden durch die Eigenviskosität des Harzes.

Das niedriger die normierte Viskosität bei einem bestimmten Füllgrad ist, um so besser läßt sich das gefüllte Harz verarbeiten. Somit ist aus Abb. 2 ersichtlich, daß das Viskositätsverhalten mit dem erfindungsgemäßen Produkt ein Optimum erreicht.

50 Der Grenzfüllgrad als Übergang von "gerade noch fließfähig" zu "stichfest" wird die Beispiele nach Abb. 2 wie folgt definiert: Die Viskosität des untersuchten Harzes ist mehr als 110 mal größer als die des ungefüllten Harzes. Unter dieser Voraussetzung wird für den Vergleichsversuch V4 der Grenzfüllgrad bei 140 Teilen Hydroxid auf 100 Teile Harz erreicht, während beim erfindungsgemäßen Produkt der Grenzwert erst bei ca. 190 Teilen Hydroxid auf 100 Teilen Harz erreicht wird.

55 Im folgenden wird das erfindungsgemäße Verfahren zur Herstellung eines gemeinen Hydroxids mit guten Füllstoffeigenschaften beschrieben. Dabei wird eine Schwingmühle eingesetzt (Typ PALLA 20 U, Fa. KHD) mit folgenden Betriebsparametern:

5

Schwingkreis:	4 - 6 $\mu\text{m}$
Drehzahl:	1400 Upm
Mahlkörper:	1/2" Cylpebs aus Keramik
Füllgrad der Mahlkörper:	ca. 66 %
Durchsatz:	40 - 60 kg/h Hydroxid.

Als Aufgabematerial wurde ein Aluminiumhydroxid mit einer mittleren Korngröße von 40 - 60  $\mu\text{m}$  gewählt, bei dem der Grobanteil über 128  $\mu\text{m}$ , max. 5 % aufwies. Nach Mahlung wurde ein Aluminiumhydroxid mit einer mittleren Korngröße von 11  $\mu\text{m}$  bei einer Kornobergrenze von 60  $\mu\text{m}$  von max. 0,5 % erhalten.

Tabelle 1

Kornverteilungen beim erfindungsgemäßen Produkt E und Vergleichsprodukten V 1 - V4						
	Fuller	E	V1	V2	V3	V4
$d_{90}$ ( $\mu\text{m}$ )	35,6	30,9	28,1	27,3	22,6	21,7
$d_{50}$ ( $\mu\text{m}$ )	11	ca.11	ca. 11	ca.11	ca.11	11
$d_{10}$ ( $\mu\text{m}$ )	0,4	1,8	2,1	2,3	2,1	4,0
B ( $\mu\text{m}$ )	5,31	4,22	3,85	3,71	3,30	2,66

## 25 Patentansprüche

1. Gemahlenes Aluminiumhydroxid mit einer mittleren Korngröße  $d_{50}$  von 10 - 15  $\mu\text{m}$ , vorzugsweise 11 - 14  $\mu\text{m}$ , dadurch gekennzeichnet, daß die Kornobergrenze bei 63  $\mu\text{m}$  mit max. 0,5 % begrenzt ist und daß die Breite B der Kornverteilung, gemessen als  $B = \sqrt{d_{90}} - \sqrt{d_{10}}$ , zwischen 4 - 5 liegt.
2. Verfahren zur Herstellung eines Aluminiumhydroxid für die Einmischung in Duroplaste, wobei übliches nach dem BAYER-Verfahren gewonnenes Aluminiumhydroxid mit einer mittleren Korngröße  $d_{50} = 40 - 60 \mu\text{m}$  mit einem Grobanteil > 125  $\mu\text{m}$  von max. 5 % gemahlen wird, dadurch gekennzeichnet, daß eine Mühle mit Mahlkörpern aus Keramik wie Kugel- oder Trommelmühle, vorzugsweise Schwingmühle eingesetzt wird.
3. Flammgeschützter Kunststoff auf Basis von Duroplasten, enthaltend gemahlenes Aluminiumhydroxid, dadurch gekennzeichnet, daß die mittlere Korngröße des Aluminiumhydroxids  $d_{50} = 10 - 15 \mu\text{m}$  beträgt, vorzugsweise  $d_{50} = 11 - 14 \mu\text{m}$  beträgt, die Kornobergrenze bei 63  $\mu\text{m}$  von max. 0,5 % liegt und das Mischungsverhältnis von Hydroxid zu Harz bei 160 - 180 : 100 Gewichtsteilen liegt bei einem Grenzfüllgrad - gemessen als Übergang von "gerade noch fließfähig" zu "stichfest" - von 110 mal höherer Viskosität als der des ungefüllten Harzes.

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50

55

Vergleich der Kornver-  
teilungen von E mit  
Konkurrenzprodukten  
 $V_1 - V_3$

E ———  
 $V_1$  - - -  
 $V_2$  - - -  
 $V_3$  - - -

Fig. 1

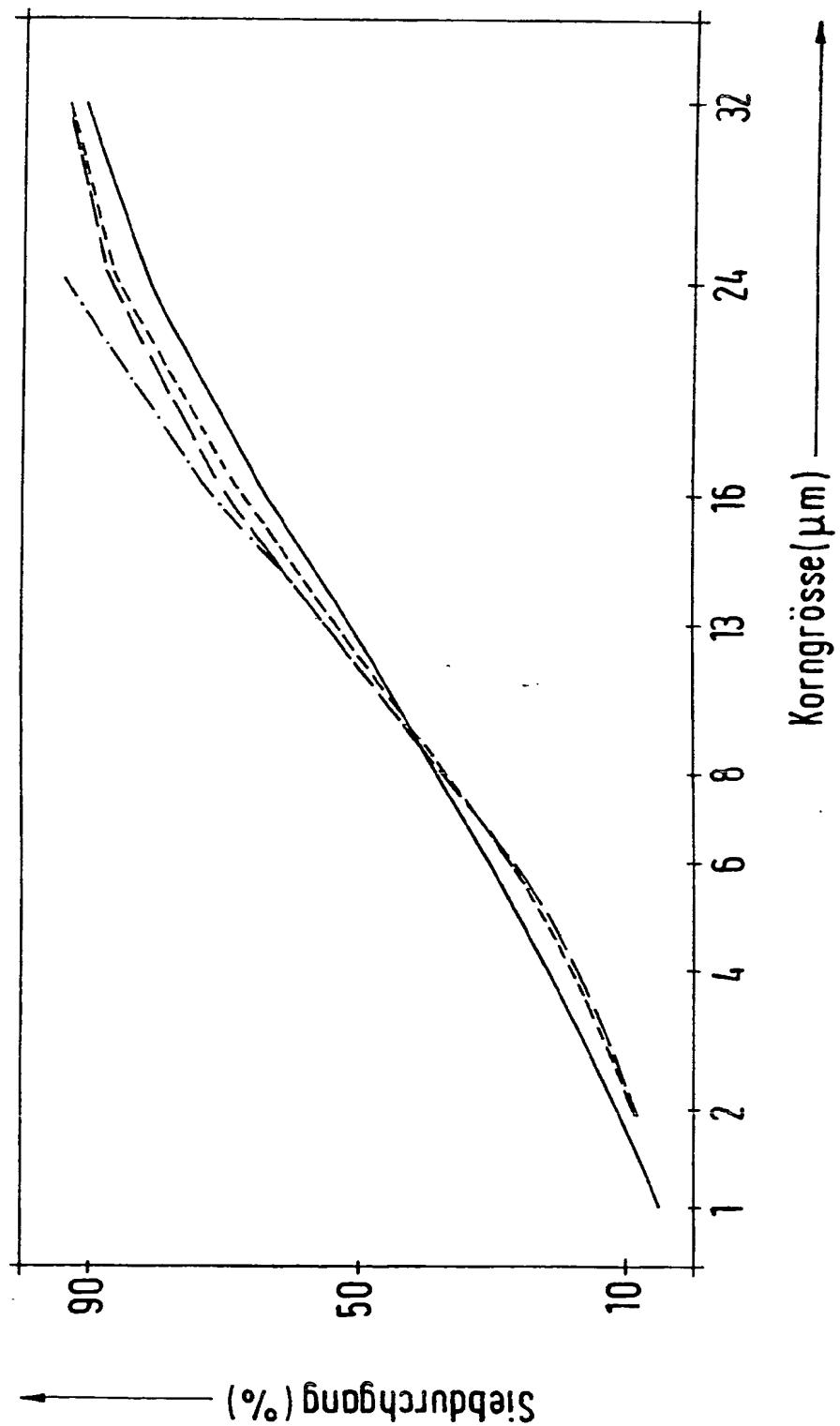
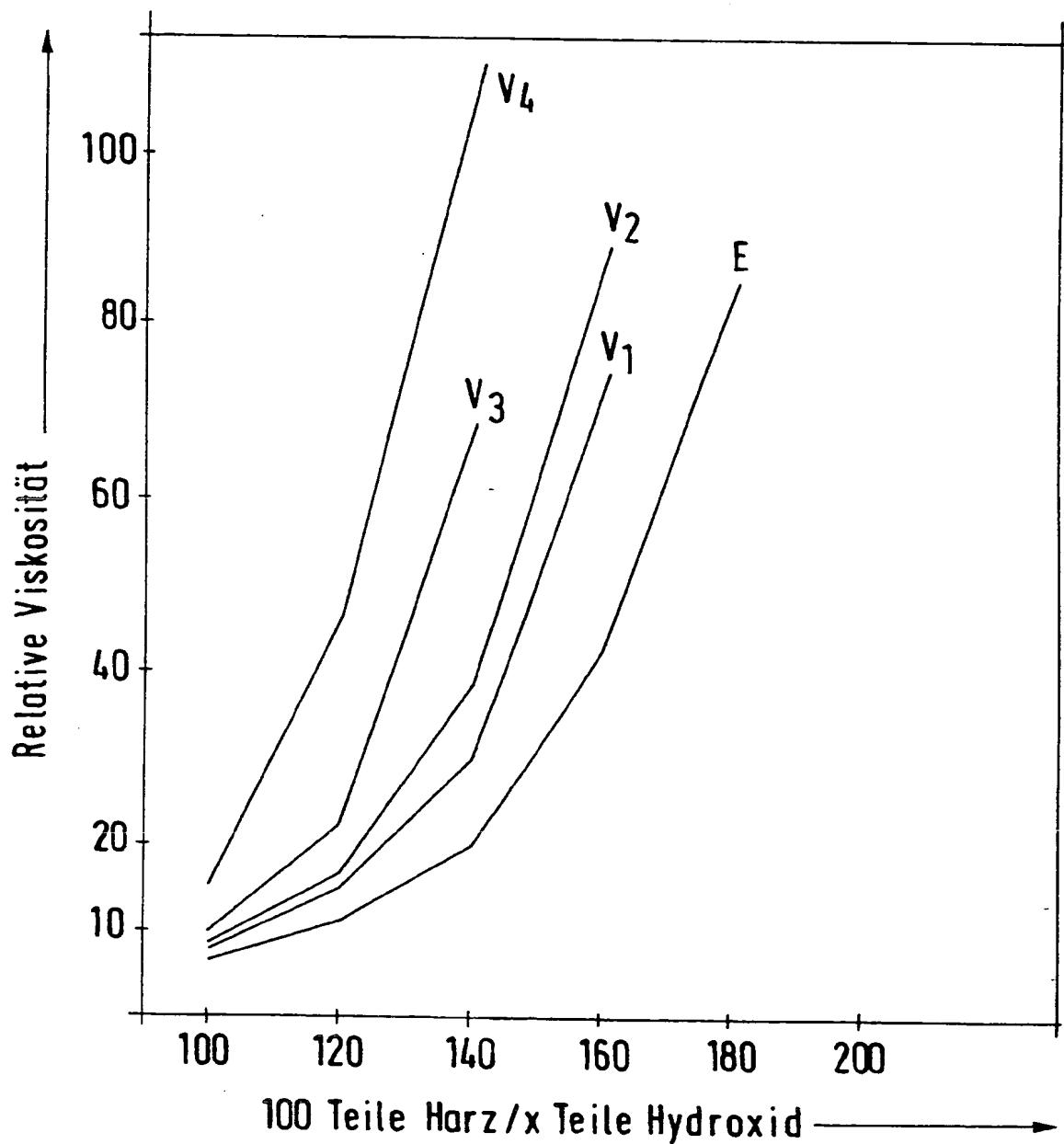


Fig.2

Viskositätsverhalten von Apyral 16 und  
Konkurrenzprodukten im UP-Harz Leguval N 22





⑫

## EUROPÄISCHE PATENTANMELDUNG

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⑰ Benannte Vertragsstaaten:  
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Recherchenberichts: 19.11.92 Patentblatt 92/47

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⑰ Veröffentlichungstag des später veröffentlichten  
Recherchenberichts: 19.11.92 Patentblatt 92/47

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⑳ Aluminiumhydroxid für die Einmischung in Kunststoff und Verfahren zu seiner Herstellung.

㉑ Bisher war es nicht möglich, mit gemahlenem Hydroxid mit einer mittleren Korngröße von 10 - 15  $\mu\text{m}$  Füllgrade von mehr als 160 Teilen Hydroxid auf 100 Teile Kunstharz zu erreichen.

umhydroxids ist dadurch gekennzeichnet, daß eine Mühle mit Mahlkörpern aus Keramik wie Kugel- oder Trommelmühle, vorzugsweise Schwingmühle, eingesetzt wird.

Es soll ein Aluminiumhydroxid zur Flammfestmachung von Kunststoffen und Verfahren zu seiner Herstellung sowie ein flammgeschützter Kunststoff auf Basis von Duroplasten entwickelt werden, wobei das Aluminiumhydroxid mit einem Füllgrad von mehr als 160 Teilen Aluminiumhydroxid auf 100 Teile Kunstharz einmischbar ist und dabei eine günstige Viskosität aufweist sowie eine glatte Oberfläche an dem daraus hergestellten Fertigteil zeigt. Das gemahlene Aluminiumhydroxid zeichnet sich dadurch aus, daß die Kornobergrenze bei 63  $\mu\text{m}$  mit max. 0,5 % begrenzt ist und daß die Breite B der Kornverteilung, gemessen als  $B = \sqrt{d_{90}} - \sqrt{d_{10}}$ , zwischen 4 - 5 liegt. Das Verfahren zur Herstellung eines Alumini-

umhydroxids ist dadurch gekennzeichnet, daß eine Mühle mit Mahlkörpern aus Keramik wie Kugel- oder Trommelmühle, vorzugsweise Schwingmühle, eingesetzt wird.

Das erfindungsgemäße Aluminiumhydroxid wird für die Einmischung in Kunststoffe vom Typ Duroplaste verwendet.



EP 91 10 7996

EINSCHLÄGIGE DOKUMENTE															
Kategorie	Kennzeichnung des Dokuments mit Angabe, soweit erforderlich, der maßgeblichen Teile	Betrift Anspruch	KLASSIFIKATION DER ANMELDUNG (Int. Cl.5)												
P, A	EP-A-0 407 595 (SHOWA DENKO KABUSHIKI) * Ansprüche 1,5,8,11 *	1,2	C01F7/02												
A	PATENT ABSTRACTS OF JAPAN vol. 14, no. 43 (C-681)(3986) 26. Januar 1990 & JP-A-1 275 422 ( SHOWA DENKO K. K. ) 6. November 1989 * Zusammenfassung *	1,2													
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A	EP-A-0 011 667 (VEREINIGTE ALUMINIUM-WERKE AG) * Anspruch 1 *	1													
A	EP-A-0 305 745 (HOECHST AG) * Ansprüche 1,12 *	3													
A	EP-A-0 276 430 (ISOBLOC GMBH) * Anspruch 1 *	3													
			RECHERCHIERTE SACHGEBIETE (Int. Cl.5)												
			C01F C08K												
<p>Der vorliegende Recherchenbericht wurde für alle Patentansprüche erstellt</p> <table border="1"> <tr> <td>Recherchemart BERLIN</td> <td>Abschlußdatum der Recherche 27 AUGUST 1992</td> <td>Prüfer CLEMENT J-P.</td> </tr> <tr> <td colspan="3">KATEGORIE DER GENANNTEN DOKUMENTE</td> </tr> <tr> <td colspan="3">           X : von besonderer Bedeutung allein betrachtet            Y : von besonderer Bedeutung in Verbindung mit einer anderen Veröffentlichung derselben Kategorie            A : technologischer Hintergrund            O : nichtschriftliche Offenbarung            P : Zwischenliteratur         </td> </tr> <tr> <td colspan="3">           T : der Erfindung zugrunde liegende Theorien oder Grundsätze            E : älteres Patentdokument, das jedoch erst am oder nach dem Anmeldedatum veröffentlicht worden ist            D : in der Anmeldung angeführtes Dokument            L : aus anderen Gründen angeführtes Dokument            &amp; : Mitglied der gleichen Patentfamilie, übereinstimmendes Dokument         </td> </tr> </table>				Recherchemart BERLIN	Abschlußdatum der Recherche 27 AUGUST 1992	Prüfer CLEMENT J-P.	KATEGORIE DER GENANNTEN DOKUMENTE			X : von besonderer Bedeutung allein betrachtet Y : von besonderer Bedeutung in Verbindung mit einer anderen Veröffentlichung derselben Kategorie A : technologischer Hintergrund O : nichtschriftliche Offenbarung P : Zwischenliteratur			T : der Erfindung zugrunde liegende Theorien oder Grundsätze E : älteres Patentdokument, das jedoch erst am oder nach dem Anmeldedatum veröffentlicht worden ist D : in der Anmeldung angeführtes Dokument L : aus anderen Gründen angeführtes Dokument & : Mitglied der gleichen Patentfamilie, übereinstimmendes Dokument		
Recherchemart BERLIN	Abschlußdatum der Recherche 27 AUGUST 1992	Prüfer CLEMENT J-P.													
KATEGORIE DER GENANNTEN DOKUMENTE															
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⑪ Veröffentlichungsnummer : **0 499 585 A1**

⑫

## EUROPÄISCHE PATENTANMELDUNG

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⑯ **Füllstoff für wärmeleitende Kunststoffe.**

⑯ Pulvriges Gemisch aus Aluminiumoxid mit Fraktionen unterschiedlicher Teilchengrösse und äusserer Gestalt, dadurch gekennzeichnet, dass es enthält :

(1) 55 bis 75 Volumen-% sphärisches  $\alpha$ -Aluminiumoxid, von dem mindestens 90 Gew.-% einen Teilchendurchmesser von 20 bis 120  $\mu\text{m}$  aufweisen,

(2) 35 bis 20 Volumen-% sphärisches Aluminiumoxid, von dem mindestens 90 Gew.-% einen Teilchendurchmesser von 3 bis 25  $\mu\text{m}$  aufweisen, und

(3) 10 bis 1 Volumen-% Aluminiumoxid mit unregelmässiger Teilchengestalt, von dem mindestens 90 Gew.-% einen Teilchendurchmesser von 1 bis 7  $\mu\text{m}$  aufweisen, wobei sich die Volumen-% zu 100 % addieren.

Das Gemisch eignet sich als Füllstoff für Kunststoffe, besonders für Giessharze, aus denen Formteile mit hoher Wärmeleitfähigkeit hergestellt werden können.

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Jouve, 18, rue Saint-Denis, 75001 PARIS

Die vorliegende Erfindung betrifft eine als Füllstoff zur Herstellung von wärmeleitenden Kunststoffen geeignete Zusammensetzung aus drei verschiedenen Fraktionen von Aluminiumoxidteilchen mit jeweils unterschiedlichen Teilchendurchmessern, eine Zusammensetzung aus einem Kunststoff und diesem Füllstoff und die Verwendung der Kunststoffzusammensetzung als Formmassen zur Herstellung von Formteilen und Verbundwerkstoffen

Es ist bekannt, dass Kunststoffe schlechte Wärmeleiter sind. Zur Verbesserung der Wärmeleitfähigkeit werden Kunststoffen daher feinteilige metallische oder mineralische Füllstoffe einverleibt. Die Verwendung von metallischen Füllstoffen ist nur möglich, wenn keine elektrischen Isoliereigenschaften gefordert sind. Als mineralische Füllstoffe werden häufig Quarz und amorphes Silica, mit denen man bei hohen Füllgraden eine thermische Leitfähigkeit bis zu etwa 2,5 W/mK, oder besonders Aluminiumoxid eingesetzt, mit dem man eine thermische Leitfähigkeit bis zu etwa 3,5 W/mK erzielen kann. Zur Vermeidung des Abriebs bei Werkzeugen werden zweckmäßig sphärische Teilchen eingesetzt. Es ist ferner bekannt, dass der Abrieb durch die Wahl von Teilchen geringer Grösse verhindert werden kann, was aber auch zu einer Verminderung des Füllgrades und damit der Wärmeleitfähigkeit führt.

In CA 112: 57551r (1990) sind thermisch leitende Polymere beschrieben, die elektrisch geschmolzenes Aluminiumoxidpulver als Füllstoff enthalten. Dieser Füllstoff ist bekannterweise abrasiv, was die Anwendungsmöglichkeiten einschränkt.

In CA 112:57894e (1990) sind Epoxidharze mit  $\alpha$ -Aluminiumoxid als Füllstoff beschrieben, die einen mittleren Teilchendurchmesser von 5 bis 60  $\mu\text{m}$  aufweisen. Der erzielbare Füllgrad und die thermische Leitfähigkeit werden als nicht ausreichend empfunden.

In CA 111: 175480u (1989) sind thermisch leitende Polymere beschrieben, die eine Mischung aus Aluminiumoxid und hauptsächlich sphärischem Korund mit einem sehr kleinen Teilchendurchmesser zwischen 5 und 10  $\mu\text{m}$  enthalten. Mit diesem Füllstoff können keine hohen Füllgrade und damit hohe thermische Leitfähigkeiten erzielt werden.

Es wurde nun gefunden, dass man sowohl den Füllgrad weiter erhöhen als auch höhere thermische Leitfähigkeiten erzielen kann, wobei die thermischen Ausdehnungskoeffizienten nahe bei denen von Metallen wie zum Beispiel Kupfer, Silber oder Gold liegen, wenn man als Füllstoff ein Gemisch von Aluminiumoxidfraktionen mit unterschiedlicher Partikelgrösse und von unterschiedlicher Gestalt verwendet. Es wurde ferner gefunden, dass mit diesem Füllstoff niedrigviskose Giessharze mit sehr hohem Füllstoffgehalt erhalten werden, die eine ausgezeichnete Giessfähigkeit und damit Verarbeitbarkeit aufweisen.

Ein Gegenstand der Erfindung ist somit ein pulvriges Gemisch aus Aluminiumoxid mit Fraktionen unterschiedlicher Teilchengrösse und äusserer Gestalt, das dadurch gekennzeichnet ist, dass es enthält:

- (1) 55 bis 75 Volumen-% sphärisches  $\alpha$ -Aluminiumoxid, von dem mindestens 90 Gew.-% einen Teilchendurchmesser von 20 bis 120  $\mu\text{m}$  aufweisen,
- (2) 35 bis 20 Volumen-% sphärisches Aluminiumoxid, von dem mindestens 90 Gew.-% einen Teilchendurchmesser von 3 bis 25  $\mu\text{m}$  aufweisen, und
- (3) 10 bis 1 Volumen-% Aluminiumoxid mit unregelmässiger Teilchengestalt, von dem mindestens 90 Gew.-% einen Teilchendurchmesser von 1 bis 7  $\mu\text{m}$  aufweisen, wobei sich die Volumen-% zu 100 % addieren.

Die Grössenverteilung der Teilchen wird mit einer Laser-Scanning-Messvorrichtung (Typ CIS der LOT GmbH, Darmstadt, Deutschland) bestimmt. Hierbei werden die Teilchen der mittleren 90 Gew.-% ohne die beiden Schwanzbereiche der Verteilungskurve erfasst. Die Volumenprozente beziehen sich auf die im pulvri gen Gemisch vorhandenen Feststoffe.

In einer bevorzugten Ausführungsform enthält das Gemisch

- a) 65 bis 75 Volumen-% der Komponente (1),
- b) 35 bis 22 Volumen-% der Komponente (2), und
- c) 7 bis 1 Volumen-% der Komponente (3),

wobei sich die Volumen-% zu 100 % addieren.

In einer bevorzugten Ausführungsform enthält das Gemisch

- a) 70 bis 75 Volumen-% der Komponente (1),
- b) 30 bis 22 Volumen-% der Komponente (2), und
- c) 7 bis 1 Volumen-% der Komponente (3),

wobei sich die Volumen-% zu 100 % addieren.

Unregelmässige Gestalt bedeutet nicht nachbehandelte Teilchen, wie sie zum Beispiel nach einem Mahl vorgang vorliegen.

Der Teilchendurchmesser von Komponente (1) beträgt bevorzugt 30 bis 100  $\mu\text{m}$ , von Komponente (2) bevorzugt 3 bis 20  $\mu\text{m}$  und von Komponente (3) bevorzugt 1 bis 5  $\mu\text{m}$ .

Die übrigen 10 Gew.-% der Komponente (1) können Teilchen mit einem Durchmesser von mehr als 120

µm und bis zu 200 µm sowie von weniger als 20 µm und bis zu 0,1 µm, der Komponente (2) können Teilchen mit einem Durchmesser von mehr als 25 µm und bis zu 40 µm sowie von weniger als 3 µm und bis zu 0,01 µm, und der Komponente (3) können Teilchen mit einem Durchmesser von mehr als 7 µm und bis zu 20 µm und weniger als 1 µm und bis zu 0,001 µm enthalten.

5 Die erfindungsgemäßen Gemische können durch Vermischen der drei Komponenten hergestellt werden. Teilchenförmige Aluminiumoxide sind bekannt und kommerziell erhältlich. Fraktionen mit definierten Bereichen der Teilchengrößen sind durch übliche Trennverfahren erhältlich. Mit den Trennverfahren können auch Fraktionen so hergestellt werden, dass der Anteil der Schwanzbereiche der Verteilungskurven vermindert oder entfernt wird. So können die drei Fraktionen im erfindungsgemäßen pulvriegen Gemisch mindestens 95 Gew.% 10 oder 100 Gew.-% Teilchen mit den zuvor definierten Teilchendurchmessern enthalten. Sphärische Teilchen können zum Beispiel durch Sinterverfahren oder Schmelzverfahren hergestellt werden. Die Herstellung verschiedener Modifikationen von Aluminiumoxidteilchen ist allgemein bekannt. Die Komponenten (2) und (3) können unterschiedliche Modifikationen aufweisen.

15 Die erfindungsgemäßen Gemische eignen sich hervorragend als Füllstoffe für Polymere, um die Wärmeleitfähigkeit zu erhöhen, wobei die Abrasivität der Zusammensetzung gering ist.

Ein weiterer Gegenstand der Erfindung ist eine Zusammensetzung, enthaltend in gleichmässiger Verteilung

- a) 10 bis 95 Gew.-% eines thermoplastischen oder strukturell vernetzten Polymeren, und
- b) 90 bis 5 Gew.-% des zuvor beschriebenen pulvriegen Gemischs.

20 Die Zusammensetzung enthält im allgemeinen bevorzugt 10 bis 90 Gew.-% Polymer und 90 bis 10 Gew.-% des pulvriegen Gemischs. Je nach Verwendungszweck kann der Gehalt des pulvriegen Gemischs im Polymer unterschiedlich hoch sein. So kann für viele Formteile, für die keine sehr hohe Wärmeleitfähigkeit gefordert ist, ein Gehalt von 5 bis 50 Gew.-%, bevorzugt 10 bis 40 Gew.-% des pulvriegen Gemischs den Anforderungen an Gebrauchsgegenstände zur Wärmeableitung genügen. Wenn eine sehr hohe Wärmeleitfähigkeit erzielt werden soll, zum Beispiel bei Klebern für die Verbindung von Metallteilen oder Giessharzen für die Umhüllung von elektrischen oder elektronischen Bauteilen, beträgt der Gehalt des pulvriegen Gemischs im allgemeinen mehr als 50 Gew.-%, bevorzugt 60 bis 90 Gew.-% und besonders 70 bis 90 Gew.-%

Bei den thermoplastischen Polymeren kann es sich zum Beispiel um die folgenden Polymeren, Copolymeren bzw. Mischungen von diesen Polymeren handeln:

- 30 1. Polymere von Mono- und Diolefinen, beispielsweise Polypropylen, Polyisobutylene, Polybuten-1, Poly-methylpenten-1, Polyisopren oder Polybutadien sowie Polymerisate von Cycloolefinen wie z.B. von Cyclopenten oder Norbornen; ferner Polyethylen (das gegebenenfalls vernetzt sein kann), z.B. Polyethylen hoher Dichte (HDPE), Polyethylen niederer Dichte (LDPE), lineares Polyethylen niederer Dichte (LLDPE).
- 35 2. Mischungen der unter 1) genannten Polymeren, z.B. Mischungen von Polypropylen mit Polyisobutylene, Polypropylen mit Polyethylen (z.B. PP/HDPE, PP/LDPE) und Mischungen verschiedener Polyethylentypen (z.B. LDPE/HDPE).
- 40 3. Copolymeren von Mono- und Diolefinen untereinander oder mit anderen Vinylmonomeren, wie z.B. Ethylen-Propylen-Copolymere, lineares Polyethylen niederer Dichte (LLDPE) und Mischungen desselben mit Polyethylen niederer Dichte (LDPE), Propylen-Buten-1-Copolymere, Propylen-Isobutylene-Copolymere, Ethylen-Buten-1-Copolymere, Ethylen-Hexen-Copolymere, Ethylen-Methylpenten-Copolymere, Ethylen-Hepten-Copolymere, Ethylen-Octen-Copolymere, Propylen-Butadien-Copolymere, Isobutylene-Isopren-Copolymere, Ethylen-Alkylacrylat-Copolymere, Ethylen-Alkylmethacrylat-Copolymere, Ethylen-Vinylacetat-Copolymere oder Ethylen-Acrylicsäure-Copolymere und deren Salze (Ionomere), sowie Terpolymere von Ethylen mit Propylen und einem Dien, wie Hexadien, Dicyclopentadien oder Ethylidennorbornen; ferner Mischungen solcher Copolymeren untereinander und mit unter 1) genannten Polymeren, z.B. Polypropylen/Ethylen-Propylen-Copolymere, LDPE/Ethylen-Vinylacetat-Copolymere, LDPE/Ethylen-Acrylicsäure-Copolymere, LLDPE/Ethylen-Vinylacetat-Copolymere und LLDPE/Ethylen-Acrylicsäure-Copolymere.
- 45 3a. Kohlenwasserstoffharze (z.B. C<sub>5</sub>-C<sub>9</sub>) inklusive hydrierte Modifikationen davon (z.B. Klebrigmacherharze).
- 50 4. Polystyrol, Poly-( $\alpha$ -methylstyrol), Poly-( $\alpha$ -methylstyrol).
- 55 5. Copolymeren von Styrol oder  $\alpha$ -Methylstyrol mit Dienen oder Acrylderivaten, wie z.B. Styrol-Butadien, Styrol-Acrylnitril, Styrol-Alkylmethacrylat, Styrol-Butadien-Alkylacrylat, Styrol-Maleinsäureanhydrid, Styrol-Acrylnitril-Methylacrylat; Mischungen von hoher Schlagzähigkeit aus Styrol-Copolymeren und einem anderen Polymer, wie z.B. einem Polyacrylat, einem Dien-Polymeren oder einem Ethylen-Propylen-Dien-Terpolymeren; sowie Block-Copolymere des Styrols, wie z.B. Styrol-Butadien-Styrol, Styrol-Isopren-Styrol, Styrol-Ethylen/Butylen-Styrol oder Styrol-Ethylen/Propylen-Styrol.
6. Ppropfopolymere von Styrol oder  $\alpha$ -Methylstyrol, wie z.B. Styrol auf Polybutadien, Styrol auf Polybutadien-Styrol- oder Polybutadien-Acrylnitril-Copolymere, Styrol und Acrylnitril (bzw. Methacrylnitril) auf Polybutadien; Styrol, Acrylnitril und Methylmethacrylat auf Polybutadien; Styrol und Maleinsäureanhydrid auf

5 Polybutadien; Styrol, Acrylnitril und Maleinsäureanhydrid oder Maleinsäureimid auf Polybutadien; Styrol und Maleinsäureimid auf Polybutadien, Styrol und Alkylacrylate bzw. Alkylmethacrylate auf Polybutadien, Styrol und Acrylnitril auf Ethylen-Propylen-Dien-Terpolymeren, Styrol und Acrylnitril auf Polyalkylacrylaten oder Polyalkylmethacrylaten, Styrol und Acrylnitril auf Acrylat-Butadien-Copolymeren, sowie deren Mischungen mit den unter 5) genannten Copolymeren, wie sie z.B. als sogenannte ABS-, MBS-, ASA- oder AES-Polymeren bekannt sind.

10 7. Halogenhaltige Polymere, wie z.B. Polychloropren, Chlorkautschuk, chloriertes oder chlorsulfonierte Polyethylen, Copolymere von Ethylen und chloriertem Ethylen, Epichlorhydrinhomo- und -copolymere, insbesondere Polymere aus halogenhaltigen Vinylverbindungen, wie z.B. Polyvinylchlorid, Polyvinylidenchlorid, Polyvinylfluorid, Polyvinylidenfluorid; sowie deren Copolymere, wie Vinylchlorid-Vinylidenchlorid, Vinylchlorid-Vinylacetat oder Vinylidenchlorid-Vinylacetat.

15 8. Polymere, die sich von  $\alpha,\beta$ -ungesättigten Säuren und deren Derivaten ableiten, wie Polyacrylate und Polymethacrylate, Polyacrylamide und Polyacrylnitrile.

10 9. Copolymere der unter 8) genannten Monomeren untereinander oder mit anderen ungesättigten Monomeren, wie z.B. Acrylnitril-Butadien-Copolymere, Acrylnitril-Alkylacrylat-Copolymere, Acrylnitril-Alkoxyalkylacrylat-Copolymere, Acrylnitril-Vinylhalogenid-Copolymere oder Acrylnitril-Alkylmethacrylat-Butadien-Terpolymeren.

20 10. Polymere, die sich von ungesättigten Alkoholen und Aminen bzw. deren Acylderivaten oder Acetalen ableiten, wie Polyvinylalkohol, Polyvinylacetat, -stearat, -benzoat, -maleat, Polyvinylbutyral, Polyallylphthalat, Polyallylmelamin; sowie deren Copolymeren mit in Punkt 1 genannten Olefinen.

11. Homo- und Copolymere von cyclischen Ethern, wie Polyalkylenglykole, Polyethylenoxyd, Polypropylenoxyd oder deren Copolymeren mit Bisglycidylethern.

25 12. Polyacetale, wie Polyoxymethylen, sowie solche Polyoxyethylene, die Comonomere, wie z.B. Ethylenoxid, enthalten; Polyacetale, die mit thermoplastischen Polyurethanen, Acrylaten oder MBS modifiziert sind.

13. Polyphenylenoxide und -sulfide und deren Mischungen mit Styrolpolymeren oder Polyamiden.

14. Polyurethane, die sich von Polyethern, Polyestern und Polybutadienen mit endständigen Hydroxylgruppen einerseits und aliphatischen oder aromatischen Polyisocyanaten andererseits ableiten, sowie deren Vorprodukte.

30 15. Polyamide und Copolyamide, die sich von Diaminen und Dicarbonsäuren und/oder von Aminocarbonsäuren oder den entsprechenden Lactamen ableiten, wie Polyamid 4, Polyamid 6, Polyamid 6/6, 6/10, 6/9, 6/12, 4/6, Polyamid 11, Polyamid 12, aromatische Polyamide ausgehend von m-Xylylendiamin und Adipinsäure; Polyamide, hergestellt aus Hexamethylendiamin und Iso- und/oder Terephthalsäure und gegebenenfalls einem Elastomer als Modifikator, z.B. Poly-2,4,4-trimethylhexamethylenterephthalamid, Poly-m-phenylen-isophthalamid. Block-Copolymere der vorstehend genannten Polyamide mit Polyolefinen, Olefin-Copolymeren, Ionomeren oder chemisch gebundenen oder gepropften Elastomeren; oder mit Polyethern, wie z.B. mit Polyethylenglykol, Polypropylenglykol oder Polytetramethylenglykol. Ferner mit EPDM oder ABS modifizierte Polyamide oder Copolyamide; sowie während der Verarbeitung kondensierte Polyamide ("RIM-Polyamidsysteme").

40 16. Polyharnstoffe, Polyimide, Polyamid-imide und Polybenzimidazole.

17. Polyester, die sich von Dicarbonsäuren und Dialkoholen und/oder von Hydroxycarbonsäuren oder den entsprechenden Lactonen ableiten, wie Polyethylenterephthalat, Polybutylenerephthalat, Poly-1,4-dimethylolcyclohexanterephthalat, Polyhydroxybenzoate, sowie Block-Polyether-ester, die sich von Polyethern mit Hydroxylendgruppen ableiten; ferner mit Polycarbonaten oder MBS modifizierte Polyester.

45 18. Polycarbonate und Polyestercarbonate.

19. Polysulfone, Polyethersulfone und Polyetherketone.

20. Polyether aus Diglycidylverbindungen, zum Beispiel Diglycidylether und Diolen, z. B. aus Bisphenol-A-Diglycidylether und Bisphenol-A.

50 21. Natürliche Polymere, wie Cellulose, Naturkautschuk, Gelatine, sowie deren polymerhomolog chemisch abgewandelte Derivate, wie Celluloseacetate, -propionate und -butyrate, bzw. die Celluloseether, wie Methylcellulose; sowie Kolophoniumharze und Derivate.

22. Mischungen (Polyblends) der vorgenannten Polymeren, wie z.B. PP/EPDM, Polyamid/EPDM oder ABS, PVC/EVA, PVC/ABS, PVC/MBS, PC/ABS, PBTP/ABS, PC/ASA, PC/PBT, PVC/CPE, PVC/Acrylate, POM/thermoplastisches PUR, PC/thermoplastisches PUR, POM/Acrylat, POM/MBS, PPO/HIPS, PPO/PA 6.6 und Copolymeren, PA/HDPE, PA/PP, PA/PPO.

55 Bei den strukturell vernetzten Polymeren kann es sich zum Beispiel um folgende Polymere handeln:

1. Vernetzte Polymere, die sich von Aldehyden einerseits und Phenolen, Harnstoff oder Melamin andererseits ableiten, wie Phenol-Formaldehyd-, Harnstoff-Formaldehyd- und Melamin-Formaldehydharze.

## 2. Trocknende und nicht-trocknende Alkydharze.

3. Ungesättigte Polyesterharze, die sich von Copolyestern gesättigter und ungesättigter Dicarbonsäuren mit mehrwertigen Alkoholen, sowie Vinylverbindungen als Vernetzungsmittel ableiten, wie auch deren halogenhaltige, schwerbrennbare Modifikationen.

5 4. Vernetzbare Acrylharze, die sich von substituierten Acrylsäureestern ableiten, wie z.B. von Epoxyacrylaten, Urethan-acrylaten oder Polyester-acrylaten.

5 5. Alkydharze, Polyesterharze und Acrylatharze, die mit Melaminharzen, Harnstoffharzen, Polyisocyanaten oder Epoxidharzen vernetzt sind.

10 6. Kautschuk auf der Basis von vernetzten Polydienenen, zum Beispiel Butadien oder Isopren; Silikonkautschuk.

7. Epoxidharze, die sich von Polyepoxiden ableiten, z.B. von Bisglycidylethem von Polyolen oder von cycloaliphatischen Diepoxiden.

Unter den vernetzten Polymeren sind vernetzte Epoxidharze bevorzugt, denen als Polyepoxide bevorzugt Glycidylverbindungen mit durchschnittlich zwei Epoxidgruppen im Molekül zu Grunde liegen. Als Glycidylverbindungen kommen vor allem solche mit zwei an ein Heteroatom (z.B. Schwefel, vorzugsweise Sauerstoff oder Stickstoff) gebundenen Glycidylgruppen,  $\beta$ -Methylglycidylgruppen oder 2,3-Epoxypropenylgruppen in Frage; genannt seien insbesondere Bis-(2,3-epoxycyclopentyl)-ether, Diglycidylether von mehrwertigen aliphatischen Alkoholen, wie 1,4-Butandiol, oder Polyalkylenglykolen, wie Polypropylenglykole; Diglycidylether von cycloaliphatischen Polyolen, wie 2,2-Bis-(4-hydroxycyclohexyl)-propan; Diglycidylether von mehrwertigen Phenolen, wie Resorcin, Bis-(p-hydroxyphenyl)-methan, 2,2-Bis-(p-hydroxyphenyl)-propan (=Diomethan), 2,2-Bis-(4'-hydroxy-3',5'-dibromphenyl)-propan, 1,3-Di-(p-hydroxyphenyl)-ethan; Di-( $\beta$ -methylglycidyl)-ether der oben angeführten zweiwertigen Alkohole oder zweiwertigen Phenole; Diglycidylester von Dicarbonsäuren, wie Phthalsäure, Terephthalsäure,  $\Delta_4$ -Tetrahydrophthalsäure und Hexahydrophthalsäure; N,N-Diglycidyllderivate von primären Aminen und Amiden und heterocyclischen, zwei N-Atome enthaltenden Stickstoffbasen, und N,N'-Diglycidyllderivate von disekundären Diamiden und Diaminen, wie N,N-Diglycidylanilin, N,N-Diglycidyltoluidin, N,N-Diglycidyl-p-aminophenyl-methyl-ether, N,N'-Dimethyl-N,N'-diglycidyl-bis-(p-aminophenyl)-methan; N',N"-Diglycidyl-N-phenyl-isocyanurat; N,N'-Diglycidylethylenhamstoff; N,N'-Diglycidyl-5,5-dimethylhydantoin, N,N'-Diglycidyl-5-isopropyl-hydantoin, N,N-Methylen-bis-(N',N'-diglycidyl-5,5-dimethylhydantoin), 1,3-Bis-(N-glycidyl-5,5-dimethylhydantoin)-2-hydroxypropan; N,N'-Diglycidyl-5,5-dimethyl-6-isopropyl-5,6-dihydro-uracil, Triglycidylisocyanurat.

30 Eine bevorzugte Gruppe von Epoxidharzen sind glycidylierte Novolake, Hydantoine, Aminophenole, Bisphenole und aromatische Diamine oder cycloaliphatische Epoxidverbindungen. Besonders bevorzugte Epoxidharze sind glycidylierte Kresolnovolake, Bisphenol-A- und Bisphenol-F-diglycidylether, Hydantoin-N,N'-bisglycid, p-Aminophenoltriglycid, Diaminodiphenylmethantetraglycid, Vinylcyclohexendioxid, 3,4-Epoxyhexylmethyl-3,4-epoxycyclohexancarboxylat oder Mischungen hiervon.

35 Geeignet sind auch vorreagierte Addukte solcher Epoxidverbindungen mit Epoxidhärtern, zum Beispiel ein Addukt aus Bisphenol-A-diglycidylether und Bisphenol-A, oder mit Oligoestern mit zwei terminalen Carboxylgruppen und Epoxiden vorreagierte Addukte.

Als Härter für Epoxidharze kommen saure oder basische Verbindungen in Frage. Als geeignete Härter sei-40 en zum Beispiel genannt: Amine, wie zum Beispiel aliphatische, cycloaliphatische oder aromatische, primäre, sekundaäre und tertiäre Amine, z. B. Ethylendiamin, Hexamethylendiamin, Trimethylhexamethylendiamin, Diethylentriamin, Triethylentetraamin, Teraethylpentaaamin, N,N-Dimethylpropenyl-1,3-diamin, N,N-Diethylpropenyl-1,3-diamin, 2,2-Bis-(4'-aminocyclohexyl)-propan, 3,3,5-Trimethyl-3-(aminomethyl)cyclohexylamin (Isophorondiamin), Mannichbasen wie z. B. 2,4,6-Tris-(dimethylaminomethyl)-phenol, m-Phenylendiamin, p-Phenylenediamin, Bis-(4-aminophenyl)-methan, Bis-(4-aminophenyl)-sulfon, Xylylendiamin; Aminoalkohole wie z. B. Aminoethanol, 1,3-Aminopropanol, Diethanolamin oder Triethanolamin; Addukte von Acylnitril an Polyalkylenpolyamine oder Monoepoxiden (Ethylenoxid, Propylenoxid) an Polyalkylenpolyamine (Diethylentriamin, Triethylentetraamin; Addukte aus einem Ueberschuss Polyaminen (Diethylentriamin, Triethylentetraamin) und Polyepoxiden wie z. B. Bisphenol-A-diglycidylethern; Polyamide, insbesondere solche aus aliphatischen Polyaminen (Diethylentriamin, Triethylentetraamin) und di- oder trimerisierten ungesättigten Fettsäuren (dimerisierte Leinöl Fettsäure, Versamid®); Dicyandiamid; Polysulfide (Thiokol®); Anilin-Formaldehyde; mehrwertige Phenole (Resorcin, 2,2-Bis-(4-hydroxyphenyl)-propan) oder Phenol-Formaldehyd-Harze; mehrbasische Carbonsäuren und ihre Anhydride, z. B. Phthalsäureanhydrid, Tetrahydrophthalsäureanhydrid, Hexahydrophthalsäureanhydrid, 4-Methylhexahydrophthalsäureanhydrid, 3,6-Endomethylen-tetrahydrophthalsäureanhydrid, 4-Methyl-3,6-endomethylen-tetrahydrophthalsäureanhydrid (Methylnadic anhydrid), 3,4,5,6,7,7-Hexachlor-endomethylen-tetrahydrophthalsäureanhydrid, Bernsteinsäureanhydrid, Adipinsäureanhydrid, Trimethyladipinsäureanhydrid, Sebacinsäureanhydrid, Maleinsäureanhydrid, Dodecylbensteinsäureanhydrid, Pyromellitsäureanhydrid, Trimellitsäureanhydrid, Benzophenontetracarbonsäureanhydrid, oder Gemische solcher

Anhydride.

Eine bevorzugte Gruppe von Härtern sind Polyamine, Novolake, Polyaminoamide und Polycarbonsäure-anhydride.

Die Epoxidharze können auch zusätzlich mit Härtungsbeschleunibern oder nur mit thermischen Härtungskatalysatoren gehärtet werden. Beispiele sind tertiäre Amine, deren Salze oder quaternäre Ammoniumverbindungen (2,4,6-Tris-(dimethylaminomethyl)phenol, Benzylidimethylamin, 2-Ethyl-4-methylimidazol, Triamylammoniumphenolat); Mono- oder Polyphenole (Phenol, Diomenthan, Salicylsäure); Bortrifluorid und seine Komplexe mit organischen Verbindungen wie z. B. Bortrifluorid-Etherkomplexe und Bortrifluorid-Amin-Komplexe ( $\text{BF}_3$ -Monoethylamin-Komplex); Phosphorsäure und Triphenylphosphit.

Härtungsbeschleuniger und Katalysatoren werden üblicherweise in einer Menge von 0,1 bis 10 Gew.-% zugegeben, bezogen auf das Epoxidharz. Härter für Epoxidharze werden im allgemeinen in äquimolaren Mengen verwendet, bezogen auf die Epoxidgruppen und funktionellen Gruppen eines Härters.

Der erfindungsgemäßen Zusammensetzung können weitere Additive zur Verbesserung der Verarbeitungseigenschaften, der mechanischen, elektrischen und thermischen Eigenschaften, der Oberflächeneigenschaften und der Lichtstabilität einverlebt sein, zum Beispiel feinteilige Füllstoffe, Verstärkerfüllstoffe, Weichmacher, Gleit- und Entformungsmittel, Haftvermittler, Antioxidantien, Wärme- und Lichtstabilisatoren, Pigmente und Farbstoffe. Werden weitere Füllstoffe und/oder Verstärkerfüllstoffe mitverwendet, so beträgt deren Höchstmenge zweckmäßig zusammen mit dem erfindungsgemäßen pulvigen Gemisch höchstens 95 Gew.-%, bevorzugt höchstens 90 Gew.-%, bezogen auf die Zusammensetzung.

Die Herstellung der erfindungsgemäßen Zusammensetzung kann nach in der Kunststofftechnik bekannten Verfahren erfolgen, zum Beispiel durch Vermischen des feinteiligen wärmeleitenden Füllstoffs mit dem Kunststoff vor, während oder nach der Herstellung, durch Plastifizieren des Kunststoffs und Vermischen mit dem Füllstoff mittels Kalandrieren, Kneten, Extrudieren oder Spritzgießen zur Herstellung von Granulaten oder Formkörpern. Es ist auch möglich, Kunststoffpulver mit dem Füllstoff trocken zu vermischen oder den Füllstoff in einer Kunststofflösung zu suspendieren und dann das Lösungsmittel zu entfernen.

Bei Duroplasten und strukturell vernetzten Polymeren wird der feinteilige Füllstoff zweckmäßig vor der Formgebung und vor dem Härteln bzw. Vernetzen zugesetzt, zum Beispiel durch gemeinsames Vermischen der Kunststoffkomponenten mit dem Füllstoff, wobei dieser zuvor einer Komponente einverlebt werden kann.

Das erfindungsgemäße pulvige Gemisch kann dem Kunststoff in Form des Gemisches selbst, in Kombination von 2 Komponenten und danach der dritten Komponente oder durch die aufeinanderfolgende Zugabe der einzelnen Komponenten einverlebt werden.

Das erfindungsgemäße Gemisch eignet sich besonders zur Herstellung von hochgefüllten Giessharzen auf der Basis von Epoxidharzen, wobei daraus hergestellte Formkörper Wärmeleitfähigkeiten bei relativ niedrigen Temperaturen von über 3,2 und sogar über 4 W/mK aufweisen können. Trotz der hohen Füllgrade ist die Viskosität der Giessharze noch so niedrig, dass sie gegebenenfalls bei Erwärmung und/oder Vibration flüssig sind und gut zu Formteilen verarbeitet werden können.

Ein weiterer Gegenstand der Erfindung ist ein Giessharz auf der Basis von Epoxidharzen, das dadurch gekennzeichnet ist, dass es in gleichmäßiger Verteilung 70 bis 90 Gew.-%, bevorzugt 75 bis 90 Gew.-% und besonders bevorzugt 80 bis 90 Gew.-% des erfindungsgemäßen pulvigen Gemisches von Aluminiumoxiden enthält.

In Frage kommende Epoxidharze sind zuvor erwähnt worden. Bevorzugte Epoxidharze sind solche auf der Basis von gegebenenfalls vorverlängerten Bisphenoldiglycidylethern, zum Beispiel Bisphenol-A- und Bisphenol-F-diglycidylether, und Polycarbonsäureanhydriden, zum Beispiel Phthalsäure- und Hydrophthalsäureanhydride als Härtern, die bevorzugt in Anwesenheit eines Härtungsbeschleunigers gehärtet werden, zum Beispiel von N-Methylimidazol.

Die erfindungsgemäße Zusammensetzung ist eine wertvolle Formmasse zur Herstellung wärmeleitender Formteile aller Art, zum Beispiel Filmen, Folien, Bändern, Fasern, Platten, Halbzeug, Formkörpern und Gehäusen. Hierbei können die für die Kunststoffverarbeitung üblichen Verfahren angewendet werden, zum Beispiel Giessen, Kalandrieren, Spritzgiessen, Spritzpressen, Extrudieren, Tiefziehen, Press- und Sinterverfahren. Die erfindungsgemäße Zusammensetzung eignet sich besonders zur Herstellung von Heizkörpern, Klebharzen und Schmelzklebern bevorzugt für die Verbindung von Metallen, sowie als wärmeleitendes Versiegelungsmaterial besonders für elektrische und elektronische Bauteile.

Ein weiterer Gegenstand der Erfindung ist die Verwendung der erfindungsgemäßen Zusammensetzung oder des erfindungsbemäßen Giessharzes zur Herstellung von wärmeleitenden Formteilen und Verbundwerkstoffen.

Ein anderer Gegenstand der Erfindung ist die Verwendung des Giessharzes als Klebharz zur Verbindung von Metallen oder als Versiegelungsmaterial für elektrische und elektronische Bauteile.

Die nachfolgenden Beispiele erläutern die Erfindung näher. Die Wärmeleitfähigkeit wird durch die ther-

sche Vergleichsmethode mit Pyroceram® 9606 als Referenzmaterial gemessen. Die Methode ist von L. C. Hulstrom et al. in "Round-Robin Testing Of Thermal Conductivity Reference Materials", Proceeding of thermal conductivity 19, October 20-23, 1985, Cookeville, Tennessee, edited by D.W. Yarbrough, beschrieben.

5 Beispiel 1:

Für die Herstellung eines Giessharzes werden folgende Aluminiumoxidfraktionen ausgewählt:

1. Gesintertes, sphärisches  $\alpha$ - $\text{Al}_2\text{O}_3$ , mittlerer Durchmesser 47  $\mu\text{m}$ , Teilchendurchmesser der mittleren 90 Gew.-% von 30 bis 100  $\mu\text{m}$ .

10 2. Kommerzielles sphärisches  $\alpha$ - und  $\delta$ - $\text{Al}_2\text{O}_3$  (Alunabeads CBA-10®, Showa Denko, Japan), mittlerer Durchmesser 9  $\mu\text{m}$ , Teilchendurchmesser der mittleren 90 Gew.-% von 3 bis 20  $\mu\text{m}$ .

3. Kommerzielles  $\text{Al}_2\text{O}_3$  (CTB 5/6FG®, Alcoa), mittlerer Durchmesser 3,5  $\mu\text{m}$ , Teilchendurchmesser der mittleren 90 Gew.-% von 1 bis 5  $\mu\text{m}$ .

71 Gew.-% (70 Vol.-%) der 1. Komponente und 28 Gew.-% (29 Vol.-%) der 2. Komponente werden in einer

15 Polypropylenflasche während 7 Stunden gerührt (Rührer mit beweglichen Rührblättern). Danach gibt man 1 Gew.-% (1 Vol.-%) der 3. Komponente zu und röhrt eine weitere Stunde.

Das pulvrig Gemisch wird bei 80 °C unter Röhren einem Epoxidgiessharz aus 50,9 Gew.-% Bisphenol-F-diglycidylether, 48,9 Gew.-% Hexahydrophthalsäureanhydrid und 0,2 Gew.-% N-Methylimidazol in gleichmässiger Verteilung einverleibt. Die Menge ist so bemessen, dass die Zusammensetzung unter Vibration noch giessfähig ist. Die Zusammensetzung wird in eine Aluminiumform gegossen und anschliessend 4 Stunden bei 80 °C und 18 Stunden bei 120 °C gehärtet. Der Gehalt an pulvrigem Gemisch wird über die Dichte bestimmt und beträgt 73 Vol.-% (89,4 Gew.-%). Der gehärtete Probenkörper weist bei 40 °C eine Wärmeleitfähigkeit von 4,05 W/mK auf.

25 Beispiel 2:

Gemäss Beispiel 1 wird ein Epoxidgiessharz mit 88 Gew.-% (70,2 Vol.-%) der folgenden Füllstoffmischung hergestellt:

30 72,9 Gew.-% (72 Vol.-%) Komponente 1. gemäss Beispiel 1;

23,1 Gew.-% (24 Vol.-%) Komponente 2. gemäss Beispiel 1;

4 Gew.-% (4 Vol.-%) Komponente 3. gemäss Beispiel 1.

Die Wärmeleitfähigkeit beträgt 3,6 W/mK.

35 Beispiel 3:

Gemäss Beispiel 1 wird ein Epoxidbiessharz mit 87,6 Gew.-% (69,3 Vol.-%) der folgenden Füllstoffmischung hergestellt:

38 73,8 Gew.-% (73 Vol.-%) Komponente 1. gemäss Beispiel 1;

22,2 Gew.-% (23 Vol.-%) Komponente 2. gemäss Beispiel 1;

4 Gew.-% (4 Vol.-%) Komponente 3. gemäss Beispiel 1.

Die Wärmeleitfähigkeit beträgt 3,3 W/mK.

Beispiel 4:

45 Gemäss Beispiel 1 wird ein Epoxidgiessharz mit 88,4 Gew.-% (70,9 Vol.-%) der folgenden Füllstoffmischung hergestellt:

59 Gew.-% (58 Vol.-%) Komponente 1. gemäss Beispiel 1;

35 Gew.-% (34 Vol.-%) Komponente 2. gemäss Beispiel 1;

7 Gew.-% (4 Vol.-%) Komponente 3. gemäss Beispiel 1.

50 Die Wärmeleitfähigkeit beträgt 3,8 W/mK.

**Patentansprüche**

55 1. Pulvriges Gemisch aus Aluminiumoxid mit Fraktionen unterschiedlicher Teilchengrösse und äusserer Gestalt, dadurch gekennzeichnet, dass es enthält:  
 (1) 55 bis 75 Volumen-% sphärisches  $\alpha$ -Aluminiumoxid, von dem mindestens 90 Gew.-% einen Teilchendurchmesser von 20 bis 120  $\mu\text{m}$  aufweisen,

5 (2) 35 bis 20 Volumen-% sphärisches Aluminiumoxid, von dem mindestens 90 Gew.-% einen Teilchen-durchmesser von 3 bis 25  $\mu\text{m}$  aufweisen, und

10 (3) 10 bis 1 Volumen-% Aluminiumoxid mit unregelmässiger Teilchengestalt, von dem mindestens 90 Gew.-% einen Teilchendurchmesser von 1 bis 7  $\mu\text{m}$  aufweisen, wobei sich die Volumen-% zu 100 % addieren.

15 2. Gemisch gemäss Anspruch 1, dadurch gekennzeichnet, dass es

- a) 65 bis 75 Volumen-% der Komponente (1),
- b) 35 bis 22 Volumen-% der Komponente (2), und
- c) 7 bis 1 Volumen-% der Komponente (3) enthält, wobei sich die Volumen-% zu 100 % addieren

20 3. Gemisch gemäss Anspruch 1, dadurch gekennzeichnet, dass es

- a) 70 bis 75 Volumen-% der Komponente (1),
- b) 30 bis 22 Volumen-% der Komponente (2), und
- c) 7 bis 1 Volumen-% der Komponente (3), enthält, wobei sich die Volumen-% zu 100 % addieren.

25 4. Gemisch gemäss Anspruch 1, dadurch gekennzeichnet, dass der Teilchendurchmesser von Komponente (1) 30 bis 100  $\mu\text{m}$ , von Komponente (2) 3 bis 20  $\mu\text{m}$  und von Komponente (3) 1 bis 5  $\mu\text{m}$  beträgt.

30 5. Zusammensetzung, enthaltend in gleichmässiger Verteilung

- a) 10 bis 95 Gew.-% eines thermoplastischen oder strukturell vernetzten Polymeren, und
- b) 90 bis 5 Gew.-% des pulvigen Gemischs gemäss Anspruch 1.

35 6. Zusammensetzung gemäss Anspruch 5, dadurch gekennzeichnet, dass sie 10 bis 90 Gew.-% Polymer und 90 bis 10 Gew.-% des pulvigen Gemischs enthält.

40 7. Zusammensetzung gemäss Anspruch 5, dadurch gekennzeichnet, dass es sich bei dem strukturell vernetzten Polymer um ein Epoxidharz handelt.

45 8. Giessharz auf der Basis von Epoxidharzen, dadurch gekennzeichnet dass es in gleichmässiger Verteilung 70 bis 90 Gew.-% des pulvigen Gemischs gemäss Anspruch 1 enthält, bezogen auf das Giessharz.

50 9. Giessharz gemäss Anspruch 8, dadurch gekennzeichnet, dass es 75 bis 90 Gew.-% des pulvigen Gemischs enthält.

55 10. Giessharz gemäss Anspruch 8, dadurch gekennzeichnet, dass es 80 bis 90 Gew.-% des pulvigen Gemischs enthält.

60 11. Giessharz gemäss Anspruch 8, dadurch gekennzeichnet, dass es als Harzkomponente eine Mischung aus Bisphenoldiglycidylethern und einem Polycarbonsäureanhydrid als Härter enthält.

65 12. Giessharz gemäss Anspruch 11, dadurch gekennzeichnet, dass es zusätzlich einen Härtungsbeschleuniger enthält.

70 13. Giessharz gemäss Anspruch 11, dadurch gekennzeichnet, dass es einen Bisphenol-A- oder Bisphenol-F-diglycidylether enthält.

75 14. Verwendung der Zusammensetzung gemäss Anspruch 5 zur Herstellung von wärmeleitenden Formteilen und Verbundkörpern.

80 15. Verwendung des Giessharzes gemäss Anspruch 8 zur Herstellung von wärmeleitenden Formteilen.

85 16. Verwendung des Giessharzes gemäss Anspruch 8 als Klebharz zur Verbindung von Metallen oder als Versiegelungsmaterial für elektrische und elektronische Bauteile.



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EINSCHLÄGIGE DOKUMENTE									
Kategorie	Kennzeichnung des Dokuments mit Angabe, soweit erforderlich, der maßgeblichen Teile	Betreff Anspruch	KLASSIFIKATION DER ANMELDUNG (Int. Cl.5)						
A	DE-A-1 745 062 (LOCKHEED AIRCRAFT CORP.) * Anspruch 1; Beispiel 1; Tabelle 1 *	1-15	C01F7/02 C08K3/22						
A	CHEMICAL ABSTRACTS, vol. 91, Columbus, Ohio, US; abstract no. 5960B, * Zusammenfassung * & JP-A-54 004 985 (NITTO ELECTRIC INDUSTRIAL CO) 12. März 1979 -----	1-12							
RECHERCHIERTE SACHGERIETE (Int. Cl.5)									
C01F C08K									
<p>Der vorliegende Recherchenbericht wurde für alle Patentansprüche erstellt</p> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 33%;">Recherchenart</td> <td style="width: 33%;">Abschlußdatum der Recherche</td> <td style="width: 34%;">Prüfer</td> </tr> <tr> <td>DEN HAAG</td> <td>02 JUNI 1992</td> <td>REEDIJK A.M.E.</td> </tr> </table> <p><b>KATEGORIE DER GENANNTEN DOKUMENTE</b></p> <p>X : von besonderer Bedeutung allein betrachtet  Y : von besonderer Bedeutung in Verbindung mit einer anderen Veröffentlichung derselben Kategorie  A : technologischer Hintergrund  O : nichtschriftliche Offenklärung  P : Zwischenliteratur</p> <p>T : der Erfindung zugrunde liegende Theorien oder Grundsätze  E : älteres Patentdokument, das jedoch erst am oder nach dem Anmeldedatum veröffentlicht worden ist  D : in der Anmeldung angeführtes Dokument  L : aus anderem Gründen angeführtes Dokument  &amp; : Mitglied der gleichen Patentfamilie, übereinstimmendes Dokument</p>				Recherchenart	Abschlußdatum der Recherche	Prüfer	DEN HAAG	02 JUNI 1992	REEDIJK A.M.E.
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(71)Applicant : DENKI KAGAKU KOGYO KK

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(72)Inventor : YOSHIDA AKIO

NAGASAKA HIDEAKI

## (54) SPHERICAL ALUMINA POWDER AND ITS PRODUCTION

### (57)Abstract:

**PROBLEM TO BE SOLVED:** To obtain a spherical alumina powder capable of forming a semiconductor sealing compound which is excellent in thermal conductivity, flowability, reliability with respect to moisture resistance and characteristics with respect to wear of a mold.

**SOLUTION:** The spherical alumina powder comprises  $\delta$ -alumina and  $\alpha$ -alumina as main crystal phases and in the X-ray diffraction data on the alumina powder, the ratio of maximum peak intensity of the  $\delta$ -alumina phase to that of the  $\alpha$ -alumina phase is 1:9 to 9:1. Also, the alumina powder has an average sphericity of  $\geq 0.90$  and a  $\leq 50$  ppm Na content and the pH of a slurry of the alumina powder in pure water, which slurry has a 20 wt% powder concentration, is 6-8. The production process comprises: spraying an aluminum hydroxide powder or a slurry of an aluminum hydroxide powder from a feed tube having a strong dispersing function into flame to form a fine powder; and collecting the fine powder at a  $\geq 500^{\circ}$  C high temperature.

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(54)【発明の名称】 球状アルミナ粉末及びその製造方法

(57)【要約】

【課題】熱伝導性、流動性、耐湿信頼性及び金型摩耗特性に優れた半導体封止材を得ることのできる球状アルミナ粉末が提供すること。

【解決手段】主結晶相が $\delta$ と $\alpha$ からなり、それぞれのX線回折における最大ピーク強度比が1:9~9:1、平均球形度が0.90以上、Na含有量が50ppm以下、しかも粉末濃度20重量%の純水スラリーのpHが6~8であることを特徴とする球状アルミナ粉末。及びその製造方法。

## 【特許請求の範囲】

【請求項1】 主結晶相が $\delta$ と $\alpha$ からなり、それぞれのX線回折における最大ピーク強度比が1:9~9:1、平均球形度が0.90以上、Na含有量が50ppm以下であり、しかも粉末濃度20重量%の純水スラリーのpHが6~8であることを特徴とする球状アルミナ粉末。

【請求項2】 水酸化アルミニウム粉末又は水酸化アルミニウム粉末のスラリーを強力な分散機能を有するフィード管から火炎中に噴霧し、得られた微粉末を500℃以上の高温で捕集することを特徴とする請求項1記載の球状アルミナ粉末の製造方法。

## 【発明の詳細な説明】

## 【0001】

【発明の属する技術分野】 本発明は、半導体封止材、各種基板用等の充填材として好適な球状アルミナ粉末及びその製造方法に関する。

## 【0002】

【従来の技術】 従来、球状アルミナ粉末は、熱伝導性、絶縁性に優れているので、半導体封止材や基板等の絶縁材料の充填材として使われている。しかしながら、球状シリカ粉末と比べると、流動性、金型摩耗特性、耐湿信頼性等が劣っているので、これらを解決しなければならない課題が球状アルミナ粉末にある。

【0003】 特に、金型摩耗特性の改善が大きな課題であり、それを球形状態の最適化により解決することの提案がある。例えば、特開平5-294613号公報には、破碎アルミナ粉を、ハロゲン化合物の存在下で加熱処理することによって、カッティングエッジのない丸みを帯びた粒子（角取り粒子）とすることが開示されている。このようして得られた角取りアルミナは、破碎形状アルミナよりも摩耗特性は確かに改善されるが、球状とは言い難いので、球状シリカ並に高度なレベルにまで改善することができない。

【0004】 一方、バイヤー法等で得られたアルミナを高温火炎中に溶射し、球状化する方法が知られている。しかし、この方法で得られた球状アルミナにおいても、摩耗特性はある程度改善されるが不十分であり、しかも原料に含まれる不純物Naの除去が困難で、数100ppm以上のNa分が残存する。充填材のNa分が多いと、例えば半導体封止材に使用した場合に耐湿信頼性が著しく低下するため、使用することができない。

【0005】 そこで、球状且つNa分の少ないアルミナ粉末の製法として、金属アルミニウムを爆発燃焼させてアルミナを製造する方法がある（特開平5-193908号公報）。この方法によって、高度に金型摩耗特性を高度に改善することができるが、Na分が少ないにもかかわらず、どういうわけか耐湿信頼性が不十分である。

## 【0006】

【発明が解決しようとする課題】 本発明は、上記に鑑み

てなされたものであり、その目的は、高度な熱伝導性（放熱性）を維持しつつ、金型摩耗特性、流動性及び耐湿信頼性を改善したアルミナ粉末、特に充填材として好適な球状アルミナ粉末を提供することである。

## 【0007】

【課題を解決するための手段】 すなわち、本発明は、主結晶相が $\delta$ と $\alpha$ からなり、それぞれのX線回折における最大ピーク強度比が1:9~9:1、平均球形度が0.90以上、Na含有量が50ppm以下であり、しかも粉末濃度20重量%の純水スラリーのpHが6~8であることを特徴とする球状アルミナ粉末である。また、本発明は、水酸化アルミニウム粉末又は水酸化アルミニウム粉末のスラリーを、強力な分散機能を有するフィード管から火炎中に噴霧し、得られた微粉末を500℃以上の高温で捕集することを特徴とする上記球状アルミナ粉末の製造方法である。

## 【0008】

【発明の実施の形態】 以下、更に詳しく本発明について説明する。

【0009】 本発明の球状アルミナは、主結晶相が $\delta$ と $\alpha$ からなり、それぞれのX線回折における最大ピーク強度比が1:9~9:1である。 $\delta$ 、 $\alpha$ 以外の低温型結晶相、例えば $\gamma$ 、 $\theta$ が多く存在すると放熱性が著しく損なわれるので、それらはできるだけ少ないほうがよく、 $\delta$ と $\alpha$ の合計で90重量%以上であることが望ましい。 $\delta$ と $\alpha$ の割合については、 $\delta$ が著しく多いと放熱性が、また $\alpha$ が著しく多いと金型摩耗特性が急激に低下するので、いずれもX線回折における最大ピーク強度比が90%をこえないと、特に $\delta$ 、 $\alpha$ 共にその最大ピーク強度比が30~70%の構成比率であることが好ましい。 $\delta$ と $\alpha$ の構成比率は、CuK $\alpha$ 線による粉末X線回折装置で得られた $\delta$ 結晶相の最大ピーク強度（2114）面と $\alpha$ 結晶相の最大ピーク強度（113）面の強度を算出し、両結晶相中に対する割合（%）から求めることができる。算出に際し、 $\delta$ 結晶相の最大ピーク強度（2114）面は $\alpha$ 結晶相の他のピーク強度と重なりあるためピーク分離が必要である。

【0010】 本発明の球状アルミナ粉末の平均球形度は、0.90以上、好ましくは0.95以上である。この値より低くなると、金型摩耗特性が急減に低下するうえに、流動性も低下する。

【0011】 平均球形度は、次に示す方法で測定される。まず、粒子像から粒子の投影面積（A）と周囲長（PM）を測定する。周囲長（PM）に対応する真円の面積を（B）とすると、その粒子の球形度は $A/B$ として表示できる。そこで試料粒子の周囲長（PM）と同一の周囲長を持つ真円を想定すると $PM = 2\pi r$ 、 $B = \pi r^2$ であるから、 $B = \pi \times (PM/2\pi)^2$ となり、個々の粒子の球形度は、球形度 $= A/B - A \times 4\pi/(PM)^2$ として算出できる。これを任意に選ばれた200

個以上の粒子について測定し、その平均値を平均球形度とする。実際の測定は、市販のフロー式粒子像分析装置を用いて行われ、数千個の粒子の体積基準の平均値が自動測定される。

【0012】本発明において、Naは原料段階から多く含まれやすい不純物であり、耐湿信頼性に悪影響を及ぼすので制御する必要がある。本発明においては、Naは50 ppm以下、好ましくは20 ppm以下に規制する必要がある。Naの規制はできる限り原料である水酸化アルミニウム粉末の段階で行うことが望ましいが、原料のNaレベル及びNa低減処理技術とコストとのバランスより、後述する本発明の球状アルミナ粉末の製造方法における捕集技術によって行うことが好ましい。

【0013】本発明が備えなければならない次の条件は、アルミナ粉末の中性度である。本発明では、アルミナ粉末濃度20重量%の純水スラリーのpHが6~8となるアルミナ粉末であることが必要である。これ以外のpHを示すアルミナ粉末は、結局のところ、金属等の陽イオン不純物、又は硝酸、硫酸、ハロゲン等の陰イオン不純物が多く含まれていることになり、耐湿信頼性に悪影響を及ぼす。

【0014】本発明の球状アルミナ粉末は、次のようにして製造することができる。

【0015】本発明で使用される原料は、水酸化アルミニウム粉末又はそのスラリーであるが、特に好ましくは、水酸化アルミニウム粉末のスラリーである。その理由は、アルミナ粉末のスラリーを原料とする場合に比較し、水酸化アルミニウム粉末は、 $\delta$ と $\alpha$ の割合とその構成比率の制御が容易であり、高球形度品が得られやすいうからである。すなわち、後述する溶射工程において、水酸化アルミニウム粉末の場合は脱水反応し、アルミナとなるが、その生成過程において順次結晶性の高いアルミナが形成されるために、 $\delta$ と $\alpha$ の割合を制御しやすくなるのに対し、アルミナの場合は、一般には $\alpha$ 結晶相タイプであり、 $\delta$ 結晶相の高い球状アルミナが得られ難いためと、 $\alpha$ 結晶相タイプは高温で安定なため、高い球形度を得るにはより高い火炎温度が必要になるためである。また、本発明において、水酸化アルミニウム粉末を原料とする他の利点は、同レベルのNa含有量にするためのNa除去が容易であることである。この理由としては、水酸化アルミニウム粉末の場合、脱水反応によって粒子表面のNaだけでなく粒内に存在するNaも水と共に除去されやすいためと考えられる。更には、アルミナに比べ水酸化アルミニウムは、焼成されていない分だけ原料費も安くなる。

【0016】本発明で使用される水酸化アルミニウム粉末のスラリーについて、更に詳述すると、スラリー濃度については特に限定されないが、概ね10~70重量%の範囲が好ましい。10重量%未満では著しく生産性が損なわれ、70重量%を越えると、原料の粒度、純度に

もよるがスラリー粘度が上昇し、輸送及び噴霧が困難となる。溶媒については水が、分散性、安全性及び経済性の点で好ましいが、原料である水酸化アルミニウム粉末を分散させることができれば、アルコール等の可燃性液体や水-アルコール等の混合溶液でもよい。スラリーの調製については、溶媒と原料粉を所定量投入し、十分分散するまで攪拌機等で混合すればよく、特別な調製法は必要としない。

【0017】本発明においては、水酸化アルミニウム粉末の $\delta$ 、 $\alpha$ アルミナ粉末への転化と球状化には溶射法が用いられる。溶射法によれば、球状化させやすい利点があるが、火炎温度を2000°C前後に高める必要があるため、球状化された粒子が合着し、球形度が低下する問題がある。そこで、本発明では、水酸化アルミニウム粉末を媒体中に分散させてスラリー状態とし、それを火炎中に微細な霧状で噴霧供給することが重要となる。噴霧方法としては、スプレードライヤーで用いられているような噴霧ノズルを利用できるが、好ましくは強力な分散機能を有するフィード管による噴射であり、湿式スラリーの噴射には二流体ノズルが好ましい。

【0018】また、上記湿式スラリーのかわりに、水酸化アルミニウム粉末を酸素、空気等の気体に分散させた乾式フィード法を用いることができる。この場合、強力な分散機能を有するフィード法で十分に分散させることが重要となり、例えばフィード管部をエゼクタ効果と高速空気流によるせん断力による分散を利用したリングノズル方式で行うことが好ましい。

【0019】火炎の形成には、水素、天然ガス、アセチレンガス、プロパンガス、ブタン等の燃料ガスと、空気、酸素等の助燃ガスとをノズルから噴射・燃焼させることによって行うことができる。火炎の温度は、2000°C程度以上にする。

【0020】火炎中に噴射された水酸化アルミニウム粉末は、高温の熱処理を受けて、 $\delta$ 、 $\alpha$ アルミナ粉末への転化と球状化が行われる。熱処理された粉末は、排ガスと共にプロワー等で吸引され、サイクロンやバグフィルターの捕集器で捕集される。その際の捕集温度は少なくとも500°Cは必要である。捕集温度を高くするほどNaの除去が容易となるので好ましいが、捕集器の材質からその上限は1100°C程度とする。捕集温度が500°C未満では、溶射でガス化したNa成分が捕集粉に付着析出しNa含有量が多くなる。また、その他の陽イオン不純物や陰イオン不純物が多く混入し、アルミナ粉末の中性度が不十分となる。

【0021】上記特開平5-193908号公報の技術では、Na分が少ないと、吸湿信頼性が低くなる原因是、この捕集温度に関係していると考えられ、本発明よりも著しく低温で捕集されているものと思われる。本発明のように、高温捕集を行うことによって、粉末濃度20重量%の純水スラリーのpHが6~8

の中性域にすることができる。

【0022】

【実施例】以下、実施例、比較例をあげて更に具体的に本発明を説明する。

【0023】燃焼炉を用いて、溶射法で球状アルミナを製造した。燃焼炉は開放型で、内炎と外炎が形成できるように、二重管構造のLPG-酸素混合型バーナーが炉頂に設けられており、そのバーナーの中心部には更にスラリー噴射用の二流体ノズルが取り付けられている。そして、二流体ノズルの中心からスラリーが、またその周囲から酸素がそれぞれ火炎に噴射される。火炎の形成は、二重管構造バーナーのそれぞれの噴射口の細孔から、外炎形成用と内炎形成用のLPG-酸素の混合ガスが噴射されることによって行われ、LPGと酸素ガス量の制御によって火炎状態が調整される。火炎を通過した熱処理物は、プロワーで捕集系に送られ、まず内壁がアルミナライニングされたサイクロンで捕集され、更にコージェライト製セラミックフィルターからなるバグフィルターで捕集される。途中の連絡配管は水冷ジャケット方式で水冷されている。また、サイクロン及びバグフィルターの前に冷却エアを吸引できる一次エア導入孔及び二次エア導入孔とその導入量を調整するバルブが設けられている。冷却水量とエア導入量の調整によってサイクロン及びバグフィルターの捕集温度が調節される。

【0024】実施例1～2 比較例1

平均粒径8 μm、Na含有量400 ppmの水酸化アルミニウム粉末（日本軽金属社製、商品名BF083）を純水に入れ、粉末濃度50重量%の湿式スラリーを調製した。これを二流体ノズル（アトマックス社製「型番BNH160S-IS」）の中心から、燃焼炉の火炎中に20kg/hの割合で噴射した。噴射には、ゲージ圧0.3MPa、ガス量約12Nm<sup>3</sup>/hの酸素ガスを使

\*用した。

【0025】一方、バーナーからは、内炎用として、LPG: 6Nm<sup>3</sup>/hと酸素ガス: 18Nm<sup>3</sup>/hの混合ガスを、外炎用として、バーナーの最外周の空隙から、LPG: 4Nm<sup>3</sup>/hと酸素ガス: 12Nm<sup>3</sup>/hの混合ガスを噴射した。連絡配管の冷却水量、一次エア導入孔及び二次エア導入孔の開度を種々操作し、粉末をサイクロンとバグフィルターで捕集した。各捕集器の捕集温度と、以下に従って測定された粉末特性の結果を表1に示す。

【0026】(1) 平均球形度

システム社製フロー式粒子像分析装置（商品名「FPIA-1000」）を用い、自動測定した。

(2) δ、αの構成比率

粉末X線回折装置を用い、δ結晶相の最大ピーク強度

〈2 1 14〉面とα結晶相の最大ピーク強度〈1 1 3〉面の強度を算出し、両結晶相中に対するδ結晶相の割合（%）を求めた。

(3) Na含有量

20 粉末の一定量を純水中に浸漬し100℃の温度で24時間放置した際に抽出されたNa<sup>+</sup>を原子吸光法にて測定した。

(4) 粉末濃度20重量%純水スラリーのpH

粉末と純水を用い、粉末濃度20重量%になるようにスラリーを調整し、1分間振とうした後、5分間静置した溶液のpHをpHメーターにて測定した。

(5) 平均粒径

コールター社製レーザー回折散乱法粒度分布測定装置（商品名「LS-230」）を用いて測定した。

【0027】

【表1】

	捕集温度 (℃)	平均球形度 (-)	δ、α構成比率 (%)	Na含有量 (ppm)	pH (-)	平均粒径 (μm)
実施例1	900	0.96	35	8	6.6	8.1
	700	0.95	68	24	7.5	3.2
実施例2	700	0.96	35	19	7.1	8.1
	550	0.95	68	48	7.8	3.2
比較例1	450	0.96	35	92	8.2	8.1
	180	0.95	68	270	8.8	3.2

(注1) 上段がサイクロン捕集品、下段がバグフィルター捕集品である。

(注2) δ、α構成比率 = δ × 100 / (δ + α)

【0028】表1より、本発明の製造条件で製造された実施例1、2の球状アルミナ粉末は、本発明で規定された全ての粉末特性を満たしていたが、500℃未満の捕

50 集温度で操業された比較例1では、Na含有量が非常に多いものであった。

【0029】実施例3 比較例2～3

バーナーの中心部に設置された湿式スラリー噴射用二流体ノズルのかわりに、リングノズル方式のフィード管を設け、テーブルフィーダーを用いて水酸化アルミニウム粉末を乾式で供給した。供給量はテーブルフィーダーの回転数を調整して20 kg/hとし、輸送用ガスとしてゲージ圧0.4 MPa、ガス量約15 Nm<sup>3</sup>/hの酸素ガスを用い、バーナー内のリングノズル方式のフィード管へ定量供給した。原料の供給法以外は、実施例1に準じて熱処理を行い、粉末を捕集した(実施例3)。次に、フィード管内のリングノズルを外したこと以外は、実施例3と同じ条件で実施した(比較例2)。更に、捕集温度をかえたこと以外は、実施例3と同じ条件で実施した(比較例3)。それらの結果を表2に示す。

## 【0030】

【表2】

	捕集温度 (°C)	平均球形 度 (-)	δ、α構 成比率 (%)	Na含有量 (ppm)	pH (-)	平均粒径 (μm)
実施例3	900	0.93	30	10	6.4	8.4
	700	0.92	60	26	7.6	3.4
比較例2	900	0.80	34	12	6.8	10.5
	700	0.81	62	28	7.6	3.5
比較例3	450	0.93	30	70	8.3	8.4
	180	0.92	60	290	8.9	3.4

(注1) 上段がサイクロン捕集品、下段がバグフィルター捕集品である。

(注2) δ、α構成比率 = δ × 100 / (δ + α)

【0031】表2より、乾式スラリーを用いても、本発明で規定された全ての粉末特性を有する球状アルミナ粉末が得られ(実施例3)、原料を強力に分散させない比較例2では平均球形度が低下し、500°C未満の捕集温度である比較例3ではNa含有量が非常に多かった。

## 【0032】実施例4

平均粒径30 μm、Na含有量300 ppmの水酸化アルミニウム粉末(日本軽金属社製、商品名BW33)を用いたこと以外は、実施例1と同様にして球状アルミナ※

※粉末を製造した。その結果を表3に示す。

## 【0033】実施例5

実施例1で使用した水酸化アルミニウム粉末を湿式ボールミルで24時間粉碎し、平均粒径1 μm、Na含有量400 ppmとしたものを用いたこと以外は、実施例1と同様にして球状アルミナ粉末を製造した。その結果を表3に示す。

## 【0034】

【表3】

	捕集温度 (°C)	平均球形 度 (-)	δ、α構 成比率 (%)	Na含有量 (ppm)	pH (-)	平均粒径 (μm)
実施例4	900	0.92	28	7	6.3	29.2
	700	0.92	56	21	7.1	4.3
実施例5	900	0.97	75	31	7.2	2.0
	700	0.95	85	45	7.7	0.8

(注1) 上段がサイクロン捕集品、下段がバグフィルター捕集品である。

(注2) δ、α構成比率 = δ × 100 / (δ + α)

【0035】表3より、原料の水酸化アルミニウム粉末の粒度を変更しても本発明の球状アルミナが得られた。

## 【0036】比較例4

水酸化アルミニウム粉末のかわりに、平均粒径20 μm、Na含有量50 ppmの金属アルミニウム粉末を用いたこと以外は、実施例1に準じて球状アルミナ粉末を製

50 した。その結果を表4に示す。

## 【0037】比較例5

水酸化アルミニウム粉末のかわりに、平均粒径15 μm、Na含有量50 ppmのαアルミニウム粉末を用いたこと以外は、実施例1に準じて球状アルミナ粉末を製造した。その結果を表4に示す。

【0038】

\* \* 【表4】

	捕集温度 (℃)	平均球 形度 (-)	δ、α構 成比率 (%)	Na含有量 (p p m)	p H (-)	平均粒径 (μ m)
比較例4	300	0.94	75	2	5.2	8.1
	150	0.95	100	7	5.4	0.9
比較例5	900	0.90	0	10	6.6	16.4
	700	0.91	0	40	6.8	4.3

(注1) 上段がサイクロン捕集品、下段がバグフィルター捕集品である。

(注2)  $\delta、\alpha$ 構成比率 =  $\delta \times 100 / (\delta + \alpha)$ 

【0039】表4より、金属アルミニウム粉末を原料に用いた比較例4では、p Hが6未満となり、また $\alpha$ アルミニウム粉末を用いた比較例5では、 $\delta$ 、 $\alpha$ の構成比率が0%となって、いずれも本発明の球状アルミニウム粉末を製造することができなかった。

【0040】本発明の球状アルミニウム粉末の充填材としての効果を確認するため、半導体封止材を調合し、熱伝導率、流動性、耐湿信頼性及び金型摩耗特性を以下に従い評価した。それらの結果を表5に示す。

【0041】半導体封止材の調合は、各実施例、各比較例のサイクロン捕集品とバグフィルター捕集品とを7:3の重量比で混合してなる充填材265.7重量部と、シランカップリング剤(γ-グリシドキシプロピルトリメトキシシラン)1.0重量部とを混合し、次いでエポキシ樹脂(クレゾールノボラック型エポキシ樹脂)2.1.6重量部、硬化剤(フェノールノボラック型エポキシ樹脂)10.9重量部、離型剤(カルナバワックス)1.0重量部及び硬化促進剤(トリフェニルホスフィン)0.2重量部を配合し、熱ロールで10分間混練した後、冷却粉碎して行った。

【0042】(6) 热伝導率

熱伝導率測定装置(アグネ社製「ARC-TC-1型」)を用い、室温において温度傾斜法で測定した。

(7) 流動性

175℃におけるスパイラルフローを測定した。

(8) 耐湿信頼性

アルミニウム配線を有する16ピンモニターICをトランジスター成形し、硬化後260℃のハンダ浴に10秒間浸漬した後、120℃、2気圧の水蒸気中で20V印加してアルミニ配線のオープン不良率(断線率)とリーク不良率(アルミニウム線間の漏れ電流値が10nA以上になった率)との和が50%以上になるまでの時間を求めた。試料個数は20個である。

(9) 金型摩耗特性

サイクロン捕集品とバグフィルター捕集品を7:3の重量比で配合して得られた上記充填材をシリコーンゴムに40体積%を配合して混練した後、フローテスターにて直径1000μmの孔が開いたアルミニウム製円板を通過させ、その広がりの大きさを測定した。なお、試料の通過量は100gとした。

【0043】

【表5】

充填材の種別	熱伝導率 (W/m・K)	流動性 (cm)	耐湿信頼性 (h)	金型摩耗特性 (μm)
実施例 1	3.3	102	140	1
実施例 2	3.2	100	110	2
実施例 3	3.3	97	130	9
実施例 4	3.5	99	160	10
実施例 5	3.0	96	90	0
比較例 1	3.2	99	20	3
比較例 2	3.4	90	120	100
比較例 3	3.2	97	10	12
比較例 4	3.3	100	40	20
比較例 5	3.5	101	120	60
比較例 6	3.4	100	150	50

## 【0044】

【発明の効果】本発明によれば、熱伝導性、流動性、耐

湿信頼性及び金型摩耗特性に優れた半導体封止材を得る

## 【0045】本発明の球状アルミナの製造方法によれ

ば、上記特性を有する球状アルミナを容易に製造するこ

とができる。

ことのできる球状アルミナ粉末が提供される。

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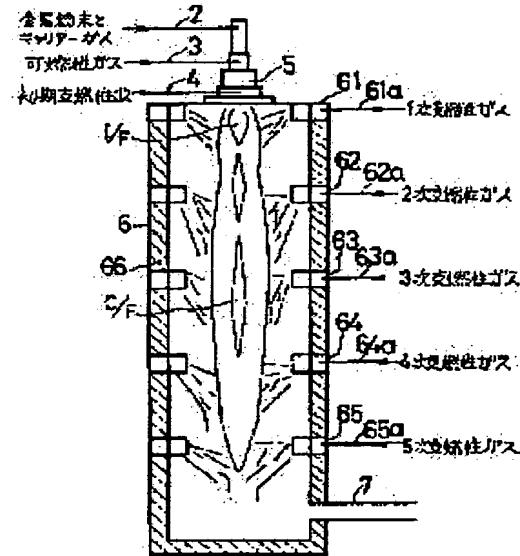
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## (54) PRODUCTION OF METAL OXIDE POWDER

### (57)Abstract:

**PURPOSE:** To independently control the particle diameter of a metal oxide powder to be produced over a wide range by controlling the supply of a combustion supporting gas in multiple stages to expand or contract the combustion flame.

**CONSTITUTION:** A combustible gas and an initial combustion supporting gas (oxygen) are supplied to a metal powder burner 5 to form an ignition flame, and a metal powder dispersed in a carrier gas is introduced into the ignition flame to form an initial flame I/F close to the burner 5. A combustion supporting gas is then introduced from feed pipes 61a,...65a to form a successive and multistage combustion flame C/F in the extending direction of the initial flame I/F. In this case, the supply and flow rate of the combustion supporting gas from the feed pipes 61a,...65a are controlled to expand or contract the combustion flame, and the particle diameter of the metal oxide powder to be produced is controlled. The particle diameter of the powder is increased as the formed combustion flame is increased in length, and the particle diameter of the powder is increased as the temp. of the combustion flame is raised.



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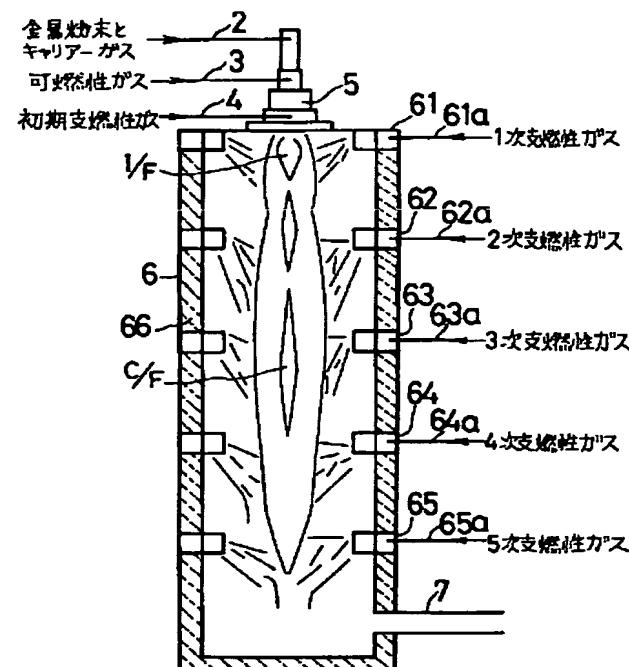
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## (54)【発明の名称】 金属酸化物粉末の製造方法

## (57)【要約】 (修正有)

【目的】 製造される金属酸化物粉末の粒径を広い範囲にわたって、単独で制御することができる金属酸化物粉末の製造方法を提供する。

【構成】 酸素含有雰囲気中で金属粉末に着火し、燃焼火炎C/Fを形成し、金属粉末を連続的に酸化燃焼させる金属酸化物粉末の製造方法において、金属粉末をキャリアーガス中に分散させる工程と、金属粉末燃焼用バーナ5によって、可燃性ガスと初期支燃性ガスから着火用火炎を形成する工程と、着火用火炎中に金属粉末を分散させたキャリアーガスを導入し、金属粉末燃焼用バーナ5付近で初期火炎I/Fを形成する工程と、初期火炎I/Fが延長する方向に、逐次的かつ多段階的燃焼火炎C/Fを形成する工程を行い、支燃性ガスの供給を制御することによって燃焼火炎C/Fを拡大または縮小し、製造される金属酸化物粉末の粒径を制御することを特徴とする金属酸化物粉末の製造方法。



## 【特許請求の範囲】

【請求項 1】酸素含有雰囲気中で金属粉末に着火し、燃焼火炎を形成し、該金属粉末を連続的に酸化燃焼させる金属酸化物粉末の製造方法において、

前記金属粉末をキャリアーガス中に分散させる工程と、金属粉末燃焼用バーナによって、可燃性ガスと初期支燃性ガスから着火用火炎を形成する工程と、

前記金属粉末を分散させた前記キャリアーガスを、前記着火用火炎中に導入し、前記金属粉末燃焼用バーナ付近で初期火炎を形成する工程と、

前記初期火炎が延長する方向に支燃性ガスを逐次的かつ多段階的に供給して前記燃焼火炎を形成する工程とを行い、

前記支燃性ガスの供給を制御することによって前記燃焼火炎を拡大または縮小し、製造される金属酸化物粉末の粒径を制御することを特徴とする金属酸化物粉末の製造方法。

## 【発明の詳細な説明】

## 【0001】

【産業上の利用分野】本発明は、金属酸化物粉末の製造方法に関する。詳しくは、製造される金属酸化物粉末の粒径を広い範囲にわたって制御することを可能にする金属酸化物粉末の製造方法に関する。

## 【0002】

【従来の技術】金属酸化物粉末の製造方法として、従来から、連続粉塵爆発の原理を応用した金属酸化物粉末の製造方法が知られている。この製造方法によって製造された金属酸化物粉末は、ゾル・ゲル法、水ガラス法、火炎加水分解法などによって製造された金属酸化物粉末とは異なり、比較的広範囲な粒度分布をもつ一次真球状微粒子で充填率が高くできるため、半導体封止材の原料、セラミックスの原料、化粧品の原料などの広い分野で利用されている。

【0003】たとえば、特開昭60-255602号公報に開示されているように、この金属酸化物粉末の製造方法は、酸素含有雰囲気中で金属粉末に着火し、燃焼火炎を形成し、金属粉末を連続的に酸化燃焼させるものである。すなわち、まず金属粉末をキャリアーガス中に分散させ、金属粉末を分散させたキャリアーガスを燃焼炉へ供給する。そして、酸素含有雰囲気中で金属粉末に着火し、燃焼火炎を形成し、金属粉末を連続的に酸化燃焼させる。すると、金属粉末の一部は、燃焼火炎中でプラズマ化する。プラズマ化した金属粉末は、冷却されると直ちに金属酸化物粉末となる。最後に、このようにして得られた金属酸化物粉末を含む排気ガスから、濾布集塵装置などを用いて金属酸化物粉末を分離、回収する。

【0004】このような金属酸化物粉末の製造方法によって製造されている金属酸化物粉末に、シリカガラス粉末がある。このシリカガラス粉末の用途の一つとして、半導体封止材の原料に応用することが考えられる。しか

し、半導体封止材の原料としてシリカガラス粉末を利用するためには、シリカガラス粉末は高い純度と広い範囲にわたる粒径をもつものでなければならない。この要求を満たすため、以下のような提案がこれまでになされている。

【0005】前記した特開昭60-255602号公報には、燃焼炉を延長して粒成長時間を長くし、かつ、金属が燃焼火炎中で液体状態を保つように外部から燃焼炉を加熱して、金属酸化物粉末の粒径を拡大する方法が記載されている。また、特開昭64-24004号公報に記載の方法は、まず、金属粉末と金属酸化物粉末の混合物をキャリアーガスとともに燃焼火炎中に供給し、燃焼させて、金属酸化物粉末を得る。この後、得られた金属酸化物粉末を循環させて、再度、金属粉末と混合し、混合物をキャリアーガスとともに燃焼火炎中に供給し、燃焼させて、粒成長させる。そして、このような操作を所定の粒径の金属酸化物粉末が得られるまで繰り返して、金属酸化物粉末の粒径を拡大するものである。なお、特開昭64-79001号公報には、金属粉末の混合物を

20 キャリアーガスとともに燃焼火炎中に供給し、燃焼させて、複合金属酸化物粉末を得るという、特開昭64-24004号公報に記載の方法と類似の方法が記載されている。

【0006】さらに、特開昭63-252910号公報、特開昭64-79004号公報や特開昭64-79005号公報には、製造される金属酸化物粉末の粒径を縮小する方法または装置が開示されている。特開昭63-252910号公報に記載の方法においては、金属粉末がキャリアーガスとともに導入された燃焼火炎の外周に冷却ガスを供給している。この冷却ガスの供給によって、金属酸化物粉末の粒成長を阻止し、製造される金属酸化物粉末の粒径を縮小している。

【0007】同様に、特開昭64-79004号公報に記載の装置においては、金属粉末をキャリアーガスとともに導入し燃焼火炎を形成する燃焼炉内に、冷却水を噴出している。この冷却水の噴出によって、金属酸化物粉末の粒成長を阻止し、製造される金属酸化物粉末の粒径を縮小している。また、特開昭64-79005号公報に記載の方法においては、金属粉末に加えて微細化助材40 をキャリアーガスとともに、燃焼火炎に導入している。この微細化助材は、燃焼火炎中で吸熱反応するもの、または、分解反応によって気体を発生するものである。この微細化助材は、燃焼火炎の温度を低下、または、金属酸化物の濃度を低下させる。微細化助材のかかる作用によって、金属酸化物粉末の粒成長を阻止し、製造される金属酸化物粉末の粒径を縮小している。

## 【0008】

【発明が解決しようとする課題】特開昭60-255602号公報や特開昭64-24004号公報に記載の方法によって、金属酸化物粉末の粒径を拡大する場合、燃

焼炉の構造を大幅に改造しなければならない、また、これに伴って燃焼炉に付帯する設備も改造、増加しなければならない。このため、金属酸化物の製造工程が複雑となり、生産性が低下してしまうという問題がある。

【0009】特開昭63-252910号公報に記載の方法や特開昭64-79004号公報に記載の装置によって、製造される金属酸化物粉末の粒径を縮小する場合、製造された金属酸化物粉末に炭素繊維などの異物が混入し易い。このため、金属酸化物粉末の品質が劣化してしまうという問題がある。また、特開昭64-79005号公報に記載の方法によって、製造される金属酸化物粉末の粒径を縮小する場合、燃焼炉の構造を大幅に改造しなければならない、また、これに伴って燃焼炉に付帯する設備も改造、増加しなければならない。このため、金属酸化物の製造工程が複雑となり、生産性が低下してしまうという問題がある。

【0010】なお、従来の技術に関する以上の説明から明らかなように、従来の技術は、製造される金属酸化物粉末の粒径の拡大または縮小のいずれかを単独で実施するものである。すなわち、製造される金属酸化物粉末の粒径の拡大および縮小の双方を、単独の方法または装置で実施することを可能とする技術は、これまで提案されたことはなかった。

【0011】本発明は、前記した従来の技術の問題点を解決するものであり、製造される金属酸化物粉末の粒径を広い範囲にわたって、単独で制御することができる金属酸化物粉末の製造方法を提供することを目的とする。

【0012】

【課題を解決するための手段】本発明は、酸素含有雰囲気中で金属粉末に着火し、燃焼火炎を形成し、該金属粉末を連続的に酸化燃焼させる金属酸化物粉末の製造方法において、前記金属粉末をキャリアーガス中に分散させる工程と、金属粉末燃焼用バーナによって、可燃性ガスと初期支燃性ガスから着火用火炎を形成する工程と、前記金属粉末を分散させた前記キャリアーガスを、前記着火用火炎中に導入し、前記金属粉末燃焼用バーナ付近で初期火炎を形成する工程と、前記初期火炎が延長する方向に支燃性ガスを逐次的かつ多段階的に供給して前記燃焼火炎を形成する工程とを行い、前記支燃性ガスの供給を制御することによって前記燃焼火炎を拡大または縮小し、製造される金属酸化物粉末の粒径を制御することを特徴とする。

【0013】本発明において使用する金属粉末は、珪素、アルミニウム、マグネシウム、チタン、ジルコニウムなどの金属粉末である。また、複合酸化物を構成するような金属粉末の混合物、たとえば、ムライトを構成するような組成の珪素粉末とアルミニウム粉末の混合物なども使用することができる。なお、高純度の金属酸化物粉末を得るために、前記したような各金属粉末の純度は、99.9%以上であるのが好ましい。さらに、金属

粉末の粒径は、燃焼を形成できる範囲の粒径分布にあればどのような粒径であってもよい。しかし、金属粉末の粒径は、400μm以下であることが好ましい。これ以上の粒径の粒子が金属粉末中に含まれると、かかる粒子を完全に酸化することができず、不完全に酸化された粒子が分離、回収された金属酸化物粉末中に含まれることになり、品質上好ましくない。なお、金属粉末の平均粒径は、数μmから数10μmの範囲にあるのがより好ましい。

10 【0014】かかる金属粉末を分散させ、金属粉末燃焼用バーナへと導入するためのキャリアーガスとして、空気、窒素、酸素、ヘリウム、アルゴンなどを使用することができ、これらのキャリアーガスのうちから、金属粉末の物性、使用する金属粉末燃焼用バーナの構造などによって適宜選択される。本発明においては、金属粉末燃焼用バーナによって可燃性ガスと初期支燃性ガスを爆発燃焼させて、着火用火炎を形成している。これらのガスのうち可燃性ガスが、金属粉末の粉塵爆発を安定して発生させるための着火源となる。可燃性ガスとして、化学式 $C_n H_{2n+2}$ で表すことができるメタン、エタン、プロパンなどの炭化水素ガス、または、水素ガスを使用することができる。また、可燃性ガスは、金属粉末の初期粉塵爆発を発生させるのに必要な最小着火エネルギーを供給できればよいので、以下に述べる燃焼火炎中で金属粉末が連続的に酸化燃焼中に、常時、可燃性ガスを供給してもよいし、燃焼火炎が安定した後は可燃性ガスの供給を停止してもよい。なお、可燃性ガスの供給量は、製造される金属酸化物粉末の粒径に若干影響するので、その供給量は、製造される金属酸化物粉末に所望の粒径に応じて適宜設定する必要がある。

20 【0015】着火用火炎中に金属粉末を分散させたキャリアーガスが導入されると、初期支燃性ガスの作用によって、金属粉末燃焼用バーナ付近で初期火炎が形成される。この初期支燃性ガスとして、酸素、空気、および、これらの混合物を使用することができ、これらの初期支燃性ガスのうちから、金属粉末の物性、使用する金属粉末燃焼用バーナの構造、使用する燃焼炉の構造などによって適宜選択される。

30 【0016】このように形成された初期火炎が延長する方向に支燃性ガスを逐次的かつ多段階的に供給して、燃焼火炎を形成する。逐次的かつ多段階的に供給される支燃性ガスは、形成される燃焼火炎の温度を上昇ないし低下させる、または、形成される燃焼火炎の長さを延長ないし短縮させる。かかる作用をする支燃性ガスの供給を制御することによって、燃焼火炎を拡大または縮小し、製造される金属酸化物粉末の粒径を制御する。この支燃性ガスとして、前記した初期支燃性ガスと同様に、酸素、空気、および、これらの混合物を使用することができ、これらの支燃性ガスのうちから、金属粉末の物性、使用する金属粉末燃焼用バーナの構造、使用する燃焼炉

の構造などによって適宜選択される。

【0017】本発明においては、金属粉末、キャリアーガス、可燃性ガス、初期支燃性ガスおよび支燃性ガスは、通常室温で燃焼炉に供給される。しかし、燃焼火炎が1000°C以上の高温となることから、燃焼炉は、アルミナなどの耐熱性材料で内張りされているのが好ましい。さらに、燃焼炉の排出側に、金属酸化物粉末回収装置や排気ガス処理装置などを介して、排風機を設け、この排風機によって排気ガスを吸引し、製造された金属酸化物粉末を金属酸化物粉末回収装置に分離、回収する。この吸引の際の圧力は、-200から-10mmAqの負圧とするのが好ましい。

#### 【0018】

【発明の作用】従来から、連続粉塵爆発の原理を応用した金属酸化物粉末の製造方法で製造される金属酸化物粉末の粒径は、金属およびその酸化物の融点、これらの溶融物の沸点や表面張力によって変化することが知られている。また、本発明者らの鋭意研究の結果によれば、製造される金属酸化物粉末の粒径は、①初期火炎中の金属粉末の濃度と不完全燃焼状態にある金属酸化物粉末の濃度、②形成された燃焼火炎の長さ、および、③燃焼火炎の温度などに、主として依存しているものと考えられる。

【0019】すなわち、初期火炎中の金属粉末の濃度と不完全燃焼状態にある金属酸化物粉末の濃度が高ければ高いほど、製造される金属酸化物粉末の粒径は拡大する。また、形成された燃焼火炎の長さが長ければ長いほど、製造される金属酸化物粉末の粒径は拡大する。また、燃焼火炎の温度が高ければ高いほど、製造される金\*

\* 属酸化物粉末の粒径は拡大する。なぜならば、以上の条件下においては、金属粉末同士、金属酸化物粉末同士または金属粉末と金属酸化物粉末の衝突頻度が増加し、燃焼火炎中の金属粉末や金属酸化物粉末の滞留時間が増加し、かつ、金属粉末と金属酸化物粉末の気化が抑制されるとともにそれらの合体が促進されるからである。以上の条件とは逆の場合、製造される金属酸化物粉末の粒径は当然に縮小する。

【0020】さらに、本発明者らの鋭意研究の結果によれば、製造される金属酸化物粉末の粒径は、金属粉末の供給量、可燃性ガスの供給量および支燃性ガスの供給量にも依存する。製造される金属酸化物粉末の粒径と、金属粉末の供給量、可燃性ガスの供給量および支燃性ガスの供給量との関係を下記の表1にまとめた。なお、金属粉末の供給量が化学量論量に近く、かつ、その供給量が多いほど、製造される金属酸化物粉末の粒径は拡大する。この逆の場合、製造される金属酸化物粉末の粒径は縮小する。しかし、従来の金属酸化物粉末の製造方法においては、使用する装置の構造などによる制約のため、金属粉末の供給量、可燃性ガスの供給量および支燃性ガスの供給量も制限されてしまう。このため、たとえば、製造されるシリカガラス粉末の粒径は、0.2から1.5μmという狭い範囲でしか制御することはできなかつた。また、たとえば、製造されるアルミナ粉末の粒径は、5から10μmという比較的狭い範囲でしか制御することはできなかつた。

#### 【0021】

##### 【表1】

金属酸化物粉末の粒径	縮小	拡大
金属粉末の供給量	少量	多量
可燃性ガスの供給量	多量	少量
支燃性ガスの供給量	多量	少量

しかし、本発明においては、金属粉末燃焼用バーナによって、可燃性ガスと初期支燃性ガスから着火用火炎を形成した後、金属粉末を分散させたキャリアーガスを着火用火炎中に導入し、金属粉末燃焼用バーナ付近で初期火炎を形成する。この後、本発明においては、初期火炎が延長する方向に支燃性ガスを逐次的かつ多段階的に供給して燃焼火炎を形成し、この支燃性ガスの供給を制御することによって、燃焼火炎を拡大または縮小し、製造される金属酸化物粉末の粒径を広い範囲にわたって、制御することを可能としている。

【0022】すなわち、本発明においては、初期火炎は燃料過剰状態なので、その中には液体状態であつてかつ

40 不完全燃焼状態の金属酸化物粉末が、高濃度で存在する。そして、かかる初期火炎が延長する方向に支燃性ガスを逐次的かつ多段階的に供給すれば、燃焼火炎が拡大する。この結果、液体状態であつてかつ不完全燃焼状態の金属酸化物粉末同士や金属粉末同士などの衝突頻度が増加し、燃焼火炎中の金属酸化物粉末や金属粉末の滞留時間が増加し、かつ、かかる金属酸化物粉末や金属粉末の気化が抑制されるとともにその合体が促進される。この結果、製造される金属粉末の粒径が拡大する。また、かかる初期火炎が延長しない方向に支燃性ガスを逐次的かつ多段階的に供給すれば、燃焼火炎が縮小する。この結果、液体状態であつてかつ不完全燃焼状態

の金属酸化物粉末同士や金属粉末同士などの衝突頻度が減少し、燃焼火炎中でのかかる金属酸化物粉末や金属粉末の滞留時間が減少し、かつ、かかる金属酸化物粉末や金属粉末の気化が促進されるとともにその合体が抑制される。この結果、製造される金属粉末の粒径が縮小する。

【0023】なお、初期火炎が延長する方向に支燃性ガスを供給するには、支燃性ガスを燃焼火炎との干渉をできるだけ避けるようにすればよい。たとえば、支燃性ガスを燃焼火炎と平行に逐次的かつ多段階的に供給する。このようにすれば、金属粉末が徐々に燃焼するので燃焼火炎を延長でき、燃焼火炎の温度も低下する。この結果、製造される金属粉末の粒径が拡大する。また、初期火炎が延長しない方向に支燃性ガスを供給するには、支燃性ガスを燃焼火炎との干渉をできるだけ助長するようすればよい。たとえば、支燃性ガスを燃焼火炎と垂直に逐次的かつ多段階的に供給する。このようにすれば、金属粉末が速やかに燃焼するので燃焼火炎を短縮でき、燃焼火炎の温度も上昇する。この結果、製造される金属粉末の粒径が縮小する。さらに、前記したような燃焼火炎との干渉をできるだけ避けるような支燃性ガスの供給方法と、燃焼火炎との干渉をできるだけ助長するような支燃性ガスの供給方法との、中間的な方法で、支燃性ガスを逐次的かつ多段階的に供給すれば、製造される金属粉末の粒径が、前記した二つの支燃性ガス供給方法で得られる二つの粒径の中間的な粒径とすることができます。

#### 【0024】

【実施例】本発明の実施例を、以下、図面を参照しながら説明する。まず、本発明の実施例で使用した金属酸化物粉末の製造装置につき説明する。図1に示すように、この製造装置は、金属粉末M/Pを供給するためのホッパ1と、ホッパ1の下部に接続された、金属粉末M/Pを分散させたキャリアーガスを着火用火炎（図示せず。）中に導入するための導入管2と、可燃性ガスを供給するための供給管3と、初期支燃性ガスを供給するための供給管4と、導入管2の排気端、供給管3の排気端および供給管4の排気端が接続された金属粉末燃焼用バーナ5と、金属粉末燃焼用バーナ5の下部に配設された燃焼炉6と、その吸気端が燃焼炉6の下部に接続された排気管7と、排気管7を介して燃焼炉6に接続された金属酸化物粉末回収装置8と、接続管9を介して金属酸化物粉末回収装置8と接続された排気ガス処理装置10と、接続管11を介して排気ガス処理装置10と接続された排風機12と、からなる。

【0025】燃焼炉6につき、図2を参照しながらさらに詳しく説明する。燃焼炉6は、円筒状をなしている。その周壁部には、上から、第1次支燃性ガス供給装置61、第2次支燃性ガス供給装置62、第3次支燃性ガス供給装置63、第4次支燃性ガス供給装置64および第

5次支燃性ガス供給装置65が、金属酸化物粉末の製造時に形成される初期火炎I/Fと燃焼火炎C/Fの周囲を取り囲むように配設されている。このように、以下で説明する実施例においては、支燃性ガス供給装置を五段階に配設したが、支燃性ガス供給装置はこれ以上、または、これ以下の多段階に配設してもよい。第1次支燃性ガス供給装置61、第2次支燃性ガス供給装置62、第3次支燃性ガス供給装置63、第4次支燃性ガス供給装置64および第5次支燃性ガス供給装置65は、それぞれ、第1次支燃性ガス供給管61a、第2次支燃性ガス供給管62a、第3次支燃性ガス供給管63a、第4次支燃性ガス供給管64aおよび第5次支燃性ガス供給管65aを介して、図示しない支燃性ガス供給源と接続している。なお、燃焼炉6の周壁部の内周面には、1000°C以上の高温に耐えるアルミナ煉瓦からなる内張り66を施してある。

（第1実施例）このように構成した金属酸化物粉末の製造装置を用いて、シリカガラス粉末を以下のように製造した。まず、可燃性ガス供給管3と初期支燃性ガス供給管4を開き、可燃性ガスとして液化石油ガス（以下、LPGという。）を、初期支燃性ガスとして酸素を、それぞれ、3.0Nm³/hr、10.0Nm³/hrなる流量で、金属粉末燃焼用バーナ5に供給し、金属粉末燃焼用バーナ5によって図示しない着火用火炎を形成した。つぎに、ホッパ1を開き、30.0kg/hrなる割合で平均粒径20.0μmの金属珪素粉末M/Pを、空気からなるキャリアーガス中に分散させた。なお、キャリアーガスは、6.0Nm³/hrなる流量で供給した。そして、かかる金属珪素粉末M/Pを分散させたキャリアーガスを、導入管2を介して、金属粉末燃焼用バーナ5に導入し、金属粉末燃焼用バーナ5によって初期火炎I/Fを形成した。

【0026】初期火炎I/Fを形成したのち、図2に示すように、第1次支燃性ガス供給管61a、第2次支燃性ガス供給管62aおよび第3次支燃性ガス供給管63aを開き、第1次支燃性ガス供給装置61、第2次支燃性ガス供給装置62および第3次支燃性ガス供給装置63に、第1次支燃性ガス、第2次支燃性ガスおよび第3次支燃性ガスを導入した後、第1次支燃性ガス供給装置61、第2次支燃性ガス供給装置62および第3次支燃性ガス供給装置63を起動し、所定の第1次支燃性ガス、第2次支燃性ガスおよび第3次支燃性ガスを所定流量で燃焼炉6内に供給し、燃焼火炎C/Fを形成した。

【0027】以上の操作において、第1次支燃性ガス、第2次支燃性ガスおよび第3次支燃性ガスは、それぞれ、酸素、酸素および空気からなり、それぞれ、40.0Nm³/hr、60.0Nm³/hr、80.0Nm³/hrなる流量で燃焼炉6内に供給した。なお、第1次支燃性ガス供給装置61、第2次支燃性ガス供給装置62および第3次支燃性ガス供給装置63は、第1次支

燃性ガス、第2次支燃性ガスおよび第3次支燃性ガスを、それぞれ、形成しようとする燃焼火炎C/Fの縦軸または燃焼炉6の中心軸に対して、俯角45度、垂直および俯角45度で供給するように調整しておいた。表2に、燃焼火炎C/Fの形成時における第1次支燃性ガス\*

\* 供給装置61、第2次支燃性ガス供給装置62および第3次支燃性ガス供給装置63の運転条件をまとめた。

【0028】

【表2】

支燃性ガス供給装置	支燃性ガスの種類	支燃性ガスの供給量*	支燃性ガスの供給方向
第1次支燃性ガス供給装置61	酸素	40.0	俯角45度
第2次支燃性ガス供給装置62	酸素	60.0	垂直
第3次支燃性ガス供給装置63	空気	80.0	俯角45度
第4次支燃性ガス供給装置64	起動せず		
第5次支燃性ガス供給装置65	起動せず		

\* 単位:  $Nm^3/h$

以上のように形成した燃焼火炎C/Fによって金属珪素粉末M/Pを連続的に酸化燃焼させた結果、含塵排ガスが発生した。排風機12を起動して、燃焼炉6から図1に示す製造装置の外部へ、排気管7、金属酸化物粉末回収装置8、接続管9、排気ガス処理装置10と接続管11を介して、発生した排気ガスを排出した。1時間後、金属珪素粉末M/Pの供給を停止し、金属酸化物粉末回収装置8のバッグフィルタ上に分離されたシリカガラス粉末を54.5kg回収した。以上の工程を経て製造されたシリカガラス粉末の平均粒径は、0.04μmであった。なお、このシリカガラス粉末は未燃焼物を含まず、その粒径分布はシャープであった。また、透過電子顕微鏡(以下、TEMという。)による観察によって、このシリカガラス粉末の形状は、真球状であることを確認した。

(比較例1) 第1実施例で用いた金属酸化物粉末の製造装置と同一の製造装置を用いて、シリカガラス粉末を第1実施例とほぼ同様に製造した。ただし、①可燃性ガスとしてLPGを、初期支燃性ガスとして酸素を、それぞれ、3.0  $Nm^3/h$ 、90.0  $Nm^3/h$ なる流量で、金属粉末燃焼用バーナ5に供給したこと、②空気からなるキャリアーガスを、6.5  $Nm^3/h$ なる流量で供給したこと、および、③全ての支燃性ガス供給装置、すなわち、第1次支燃性ガス供給装置61、第2次支燃性ガス供給装置62、第3次支燃性ガス供給装置63、第4次支燃性ガス供給装置64および第5次支燃性ガス供給装置65を、全く運転しなかったこと、以上三つの条件を第1実施例のそれとは異なる条件として、シリカガラス粉末を製造した。

【0029】以上のような製造条件下で、金属珪素粉末

M/Pを連続的に酸化燃焼させた結果、シリカガラス粉末を53.7kg回収した。以上の工程を経て製造されたシリカガラス粉末の平均粒径は、0.20μmであった。これは、第1実施例によって製造されたシリカガラス粉末の平均粒径の5倍に拡大したものであった。このように平均粒径が拡大したのは、第1次支燃性ガス供給装置61、第2次支燃性ガス供給装置62および第3次支燃性ガス供給装置63を、第1実施例におけるそれのように、運転しなかったことに起因するものであることは明らかである。なお、このシリカガラス粉末の粒径分布は、シャープであること、かつ、TEMによる観察によって、このシリカガラス粉末の形状は、真球状であることを確認した。しかし、このシリカガラス粉末は未燃焼物を多量に含み、半導体封止材などの原料として好ましいものではなかった。

30 (第2実施例) 第1実施例で用いた金属酸化物粉末の製造装置と同一の製造装置を用いて、シリカガラス粉末を第1実施例とほぼ同様に製造した。ただし、①可燃性ガスとしてLPGを、初期支燃性ガスとして酸素を、それ

40 ぞれ、0.2  $Nm^3/h$ 、10.0  $Nm^3/h$ なる流量で、金属粉末燃焼用バーナ5に供給したこと、②50 0.0kg/hなる割合で平均粒径20.0μmの金属珪素粉末M/Pを、空気からなるキャリアーガス中に分散させたこと、③空気からなるキャリアーガスを、7.0  $Nm^3/h$ なる流量で供給したこと、および、④全ての支燃性ガス供給装置、すなわち、第1次支燃性ガス供給装置61、第2次支燃性ガス供給装置62、第3次支燃性ガス供給装置63、第4次支燃性ガス供給装置64および第5次支燃性ガス供給装置65を、表3にまとめるように運転したこと、以上四つの条件を第1実

施例のそれとは異なる条件として、シリカガラス粉末を  
製造した。

\* 【0030】  
\* 【表3】

支燃性ガス供給装置	支燃性ガスの種類	支燃性ガスの供給量*	支燃性ガスの供給方向
第1次支燃性ガス供給装置61	酸素	10.0	俯角45度
第2次支燃性ガス供給装置62	酸素	10.0	平行
第3次支燃性ガス供給装置63	酸素	10.0	平行
第4次支燃性ガス供給装置64	酸素	10.0	俯角45度
第5次支燃性ガス供給装置65	酸素	10.0	俯角45度

\*単位:  $Nm^3/h$

以上のような製造条件下で、金属珪素粉末M/Pを連続的に酸化燃焼させた結果、シリカガラス粉末を57.8 kg回収した。以上の工程を経て製造されたシリカガラス粉末の平均粒径は、4.50  $\mu m$ であった。なお、このシリカガラス粉末は未燃焼物を含まず、その粒径分布は、1  $\mu m$ と5  $\mu m$ に二つのピークをもつものであった。また、TEMによる観察によって、このシリカガラス粉末の形状は、真球状であることを確認した。

(比較例2) 第1実施例で用いた金属酸化物粉末の製造装置と同一の製造装置を用いて、シリカガラス粉末を第1実施例とほぼ同様に製造した。ただし、①可燃性ガスとしてLPGを、初期支燃性ガスとして酸素を、それぞれ、0.2  $Nm^3/h$ 、50.0  $Nm^3/h$ なる流量で、金属粉末燃焼用バーナ5に供給したこと、②50.0 kg/hなる割合で平均粒径20.0  $\mu m$ の金属珪素粉末M/Pを、空気からなるキャリアーガス中に分散させたこと、③空気からなるキャリアーガスを、7.0  $Nm^3/h$ なる流量で供給したこと、および、④全ての支燃性ガス供給装置、すなわち、第1次支燃性ガス供給装置61、第2次支燃性ガス供給装置62、第3次支燃性ガス供給装置63、第4次支燃性ガス供給装置64および第5次支燃性ガス供給装置65を、全く運転しなかったこと、以上四つの条件を第1実施例のそれとは異なる条件として、シリカガラス粉末を製造した。

【0031】以上のような製造条件下で、金属珪素粉末M/Pを連続的に酸化燃焼させた結果、シリカガラス粉末を57.0 kg回収した。以上の工程を経て製造されたシリカガラス粉末の平均粒径は、2.0  $\mu m$ であった。これは、第2実施例によって製造されたシリカガラ

ス粉末の平均粒径の4/9に縮小したものであった。このように平均粒径が縮小したのは、第1次支燃性ガス供給装置61、第2次支燃性ガス供給装置62、第3次支燃性ガス供給装置63、第4次支燃性ガス供給装置64および第5次支燃性ガス供給装置65を、第2実施例におけるそれのように、運転しなかったことに起因するものであることは明らかである。

【0032】なお、このシリカガラス粉末は未燃焼物を多量に含み、半導体封止材などの原料として好ましいものではなかった。

(第3実施例) 第1実施例で用いた金属酸化物粉末の製造装置と同一の製造装置を用いて、アルミナ粉末を第1実施例とほぼ同様に製造した。ただし、①可燃性ガスとしてLPGを、初期支燃性ガスとして酸素を、それぞれ、2.0  $Nm^3/h$ 、40.0  $Nm^3/h$ なる流量で、金属粉末燃焼用バーナ5に供給したこと、②20.0 kg/hなる割合で平均粒径20.0  $\mu m$ の金属アルミニウム粉末M/Pを、窒素からなるキャリアーガス中に分散させたこと、および、③窒素からなるキャリアーガスを、6.0  $Nm^3/h$ なる流量で供給したこと、以上三つの条件を第1実施例のそれとは異なる条件として、アルミナ粉末を製造した。なお、第1次支燃性ガス供給装置61、第2次支燃性ガス供給装置62および第3次支燃性ガス供給装置63を、表4にまとめるように、第1実施例のそれらの運転条件と同一の条件下で運転した。

【0033】  
【表4】

支燃性ガス供給装置	支燃性ガスの種類	支燃性ガスの供給量*	支燃性ガスの供給方向
第1次支燃性ガス供給装置61	酸素	40.0	俯角45度
第2次支燃性ガス供給装置62	酸素	60.0	垂直
第3次支燃性ガス供給装置63	空気	80.0	俯角45度
第4次支燃性ガス供給装置64	起動せず		
第5次支燃性ガス供給装置65	起動せず		

\*単位:  $Nm^3/h r$

以上のような製造条件下で、金属アルミニウム粉末M/Pを連続的に酸化燃焼させた結果、アルミナ粉末を34.0 kg回収した。以上の工程を経て製造されたアルミナ粉末の平均粒径は、0.20  $\mu m$ であった。なお、このアルミナ粉末は未燃焼物を含まず、その粒径分布はシャープであった。また、TEMによる観察によって、このアルミナ粉末の形状は、真球状であることを確認した。

(第4実施例) 第1実施例で用いた金属酸化物粉末の製造装置と同一の製造装置を用いて、アルミナ粉末を第1実施例とほぼ同様に製造した。ただし、①可燃性ガスとしてLPGを、初期支燃性ガスとして酸素を、それぞれ、0.4  $Nm^3/h r$ 、15.0  $Nm^3/h r$ なる流量で、金属粉末燃焼用バーナ5に供給したこと、②\*

\* 0.0 kg/h rなる割合で平均粒径40.0  $\mu m$ の金属アルミニウム粉末M/Pを、窒素からなるキャリアーガス中に分散させたこと、③窒素からなるキャリアーガスを、6.0  $Nm^3/h r$ なる流量で供給したこと、および、④全ての支燃性ガス供給装置、すなわち、第1次支燃性ガス供給装置61、第2次支燃性ガス供給装置62、第3次支燃性ガス供給装置63、第4次支燃性ガス供給装置64および第5次支燃性ガス供給装置65を、表5にまとめるように運転したこと、以上四つの条件を第1実施例のそれとは異なる条件として、アルミナ粉末を製造した。

【0034】

【表5】

支燃性ガス供給装置	支燃性ガスの種類	支燃性ガスの供給量*	支燃性ガスの供給方向
第1次支燃性ガス供給装置61	酸素	10.0	俯角45度
第2次支燃性ガス供給装置62	酸素	10.0	俯角45度
第3次支燃性ガス供給装置63	酸素	10.0	俯角45度
第4次支燃性ガス供給装置64	酸素	10.0	俯角45度
第5次支燃性ガス供給装置65	酸素	10.0	俯角45度

\*単位:  $Nm^3/h r$

以上のような製造条件下で、金属アルミニウム粉末M/Pを連続的に酸化燃焼させた結果、アルミナ粉末を32.5 kg回収した。以上の工程を経て製造されたアルミナ粉末の平均粒径は、18.5  $\mu m$ であった。なお、このアルミナ粉末は未燃焼物を含まず、その粒径分布は、0.8  $\mu m$ と15  $\mu m$ に二つのピークをもつもので

50 あった。また、TEMによる観察によって、このアルミナ粉末の形状は、真球状であることを確認した。

【0035】

【発明の効果】以上詳述したように、本発明においては、金属粉末燃焼用バーナによって、可燃性ガスと初期支燃性ガスから着火用火炎を形成した後、金属粉末を分

散させたキャリアーガスを着火用火炎中に導入し、金属粉末燃焼用バーナ付近で初期火炎を形成する。この後、本発明においては、初期火炎が延長する方向に支燃性ガスを逐次的かつ多段階的に供給して燃焼火炎を形成し、この支燃性ガスの供給を制御することによって、燃焼火炎を拡大または縮小し、製造される金属酸化物粉末の粒径を広い範囲にわたって、制御することを可能としている。

【0036】したがって、本発明によれば、金属粉末の供給量、可燃性ガスの供給量および支燃性ガスの供給量などの制御、金属粉末燃焼用バーナの構造を大幅に改造することなく、さらに、炭素繊維などの異物を混入させ易い冷却水などの供給を行うことなく、製造される金属酸化物粉末の粒径を広い範囲にわたって、単一の方法または装置で、拡大および縮小することができる。すなわち、本発明は、従来の設備空間、生産時間および生産性に、影響を与えることなく、製造される金属酸化物粉末の粒径を広い範囲にわたって制御することができるので、非常に有利である。

【0037】また、本発明は、従来の技術と同様に、連続粉塵爆発の原理を応用した金属酸化物の製造方法であり、大気圧下で実施することができるので、単純な製造工程で短時間に大量の金属酸化物粉末を製造することができ、装置を簡素化でき、かつ、初期費用および運転費用を節約することができる。さらに、本発明によるシリカガラス粉末の製造においては、製造されるシリカガラス粉末の粒径を、0.02から5.0  $\mu\text{m}$ という広い範囲にわたって制御することができる。また、本発明によるアルミナ粉末の製造においては、製造されるアルミナ粉末の粒径を、0.2から20.0  $\mu\text{m}$ という広い範囲\*30

\*にわたって制御することができる。したがって、本発明によって製造された金属酸化物粉末は、高純度および低原価が要求される、半導体封止材の原料、セラミックスの原料、化粧品の原料などの広い分野において、非常に有用である。なお、本発明によって製造された金属酸化物粉末は、その形状が真球であるうえ、その粒径を広い範囲にわたって制御可能であるので、特に、半導体封止材の原料、各種充填材の原料などの流動性の向上などに大きな寄与をすることが期待できる。

#### 【図面の簡単な説明】

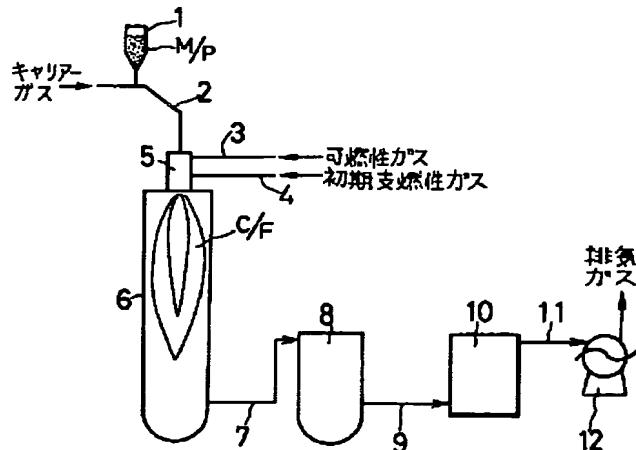
【図1】本発明の金属酸化物粉末の製造方法の実施例で使用した金属酸化物粉末の製造装置のブロック図である。

【図2】本発明の金属酸化物粉末の製造方法の実施例で使用した金属酸化物粉末の製造装置の燃焼炉の模式的な断面図である。

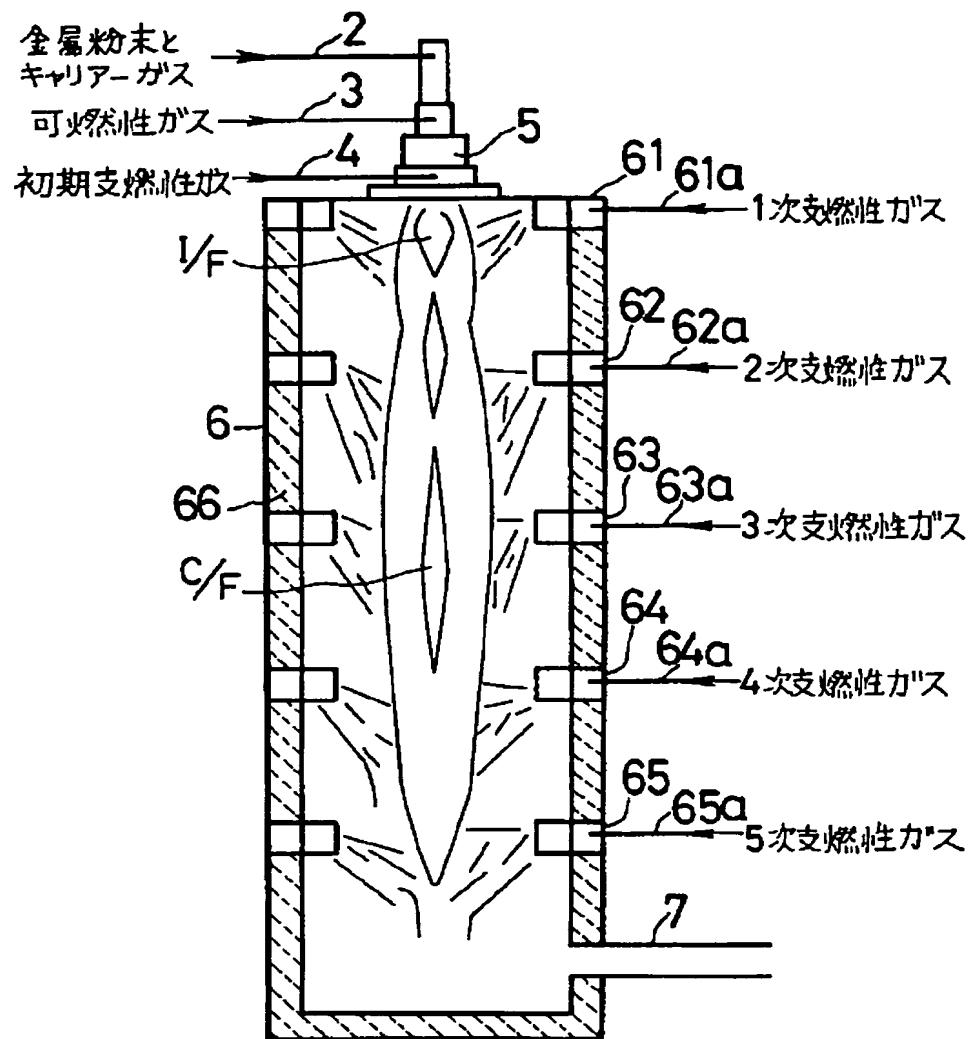
#### 【符号の説明】

1：ホッパ 2：導入管、3：可燃性ガス供給管、4：初期支燃性ガス供給管、5：金属粉末燃焼用バーナ、6：燃焼炉、6 1：第1次支燃性ガス供給装置、6 2：第2次支燃性ガス供給装置、6 3：第3次支燃性ガス供給装置、6 4：第4次支燃性ガス供給装置、6 5：第5次支燃性ガス供給装置 6 1 a：第1次支燃性ガス供給管、6 2 a：第2次支燃性ガス供給管、6 3 a：第3次支燃性ガス供給管、6 4 a：第4次支燃性ガス供給管、6 5 a：第5次支燃性ガス供給管、6 6：内張り、7：排気管、8：金属酸化物粉末回収装置、9：接続管、10：排気ガス処理装置、11：接続管、12：排風機、M/P：金属粉末、I/F：初期火炎、C/F：燃焼火炎

【図1】



【図2】



フロントページの続き

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## (54) EPOXY RESIN COMPOSITION FOR SEALING SEMICONDUCTOR

### (57)Abstract:

**PURPOSE:** To provide a moisture-resistant epoxy resin composition for sealing a semiconductor without a gap left at the interface with silica so as to elongate the life of a surface mounting IC.

**CONSTITUTION:** Epoxy resin composition for sealing a semiconductor contains surface modifying silica which is substantially mechanochemically reacted substantially to be pulverized in the presence of surface treatment agent.

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### LEGAL STATUS

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(54)【発明の名称】 半導体封止用エポキシ樹脂組成物

(57)【要約】

【目的】 シリカ界面に隙間のない半導体プラスチック封止が可能で、耐湿性、半田後耐湿性に優れるエポキシ樹脂封止により、表面実装型ICの寿命を高めることができ可能な半導体封止用エポキシ樹脂組成物を提供する。

【構成】 半導体封止用エポキシ樹脂組成物が、表面処理剤の存在下に実質的に粉碎を伴うメカノケミカル反応処理を施した表面改質シリカを含む。

## 【特許請求の範囲】

【請求項1】 表面処理剤の存在下に実質的に粉碎を伴うメカノケミカル反応処理を施した表面改質シリカを含むことを特徴とする半導体封止用エポキシ樹脂組成物。

## 【発明の詳細な説明】

## 【0001】

【産業上の利用分野】 本発明は、半導体封止用エポキシ樹脂組成物に関し、更に詳しくは、表面実装型半導体のプラスチック封止等に好ましく用いられる半導体封止用エポキシ樹脂組成物に関する。

## 【0002】

【従来の技術】 近年の技術の進歩に伴い、現在では半導体はLSI、VLSIと呼ばれる高集積化されたものになっている。この高集積度半導体素子はその外部環境から保護すべく合成樹脂組成物で封止されている。この合成樹脂組成物はエポキシ樹脂、硬化剤を主体とする有機樹脂、シリカを主体とする無機充填剤等からなり、これらを単に混合、混練して半導体の封止に使用している。この合成樹脂組成物を硬化した時に、シリカと他の成分とは単に物理的な結合状態にある。このようにシリカと他の成分との結合が物理的になる理由の一つとして、通常使用されるシリカ、例えば石英を粉碎して得られる結晶シリカあるいは石英を熔融、粉碎して得られる熔融シリカ等の表面には反応性官能基であるシラノールがほとんどないために、化学的な結合が生じ得ないことが挙げられる。

【0003】 このように従来の合成樹脂組成物を使用して半導体を封止した場合には、シリカと他の成分とが単に物理的に結合しているので、シリカ界面に隙間が生じ易く、このため容易に水が侵入し配線を腐食させる。即ち、半導体の信頼性を低下させるという問題があった。特に最近は高密度実装化の面から、パッケージは小型、薄型化した表面実装の傾向にあり、したがって、水の侵入経路が短くなったり、あるいは半田付け温度(約260℃)までパッケージ全体が加熱されることによりシリカ界面の隙間が大きくなりパッケージクラックを生じるといった問題が増加している。

【0004】 半導体への水の侵入は、また樹脂中を伝わっても行われるが、これは気体の水の拡散による侵入であり、空隙からの液体の水の侵入とは異なる。即ち、前者の場合は侵入速度は極めて遅く又電荷移動媒体としての作用も小さいため配線の腐食に対する影響は小さいが、後者の場合はその影響が顕著であり、半導体の信頼性が損なわれていた。

【0005】 また、特開昭62-12609号公報には熔融球状シリカを強力剪断操作によりメカノケミカル反応処理に付すことが記載されている。この強力剪断操作において粉碎が実質的に生じないようになると必要であり、剪断操作には注意を要するとされている(第4頁左上欄)。

## 【0006】

【発明が解決しようとする課題】 本発明は、このような問題点に鑑みてなされたものであって、半導体への水の侵入を防止し、半導体の信頼性を高める半導体封止用エポキシ樹脂組成物に関する。

## 【0007】

【課題を解決するための手段】 即ち、本発明は表面処理剤の存在下に実質的に粉碎を伴うメカノケミカル反応処理を施した表面改質シリカを含むことを特徴とする半導体封止用エポキシ樹脂組成物からなる。

【0008】 本発明の半導体封止用エポキシ樹脂組成物は、所定の表面処理剤の存在下に実質的に粉碎を伴うメカノケミカル反応処理を施した表面改質シリカを、エポキシ樹脂及び硬化剤に配合することにより製造することができる。

【0009】 該メカノケミカル反応処理を施した表面改質シリカは、以下に示すようにして製造される。

【0010】 まず、原料として使用するシリカは、特に制限はなく、結晶シリカあるいは熔融シリカのいづれであってもよく、また、該シリカ形状は破碎状であっても、球状であってもよい。

【0011】 また、本発明の表面処理剤は、エポキシ樹脂と反応する官能基もしくは相溶する基(例えば、エポキシ基、カルボキシル基、水酸基、フェニル基等)、及びシリカと反応する官能基(例えば、-Si(OR)<sub>3</sub>)。

(ここで、nは1~3の整数を示し、RはH又は炭化水素残基を示す。)、-SiH、ビニル基等)を有するものであればいづれでもよく、例えばカップリング剤(例えば、エポキシシラン、アミノシラン、ビニルシラン等が挙げられ、より具体的には、例えばγ-グリシドキシプロピルトリメトキシシラン、γ-グリシドキシプロピルメチルジエトキシシラン、β-(3,4-エポキシシクロヘキシル)エチルトリメトキシシラン、γ-アミノプロピルトリエトキシシラン、N-β(アミノエチル)γ-アミノプロピルトリメトキシシラン、N-β(アミノエチル)γ-アミノプロピルメチルジメトキシシラン、ビニルトリメトキシシラン、フェニルトリメトキシシラン、ジフェニルメトキシシラン等が挙げられる)、ラジカル重合が可能なモノマー(例えば、アクリル酸メチル、アクリル酸エチル、アクリル酸ブチル、アクリル酸フェニル等のアクリル系モノマー、メタクリル酸メチル(MMA)、メタクリル酸エチル、メタクリル酸ブチル、メタクリル酸ビニル、メタクリル酸グリシジル等のメタクリル系モノマー及びスチレン等)等が挙げられる。

【0012】 本発明におけるメカノケミカル反応処理は、上記の表面処理剤をシリカの粉碎工程時に添加することにより、粉碎時に生成したラジカルや発生期のシラノールと反応させシリカ表面に化学的に結合させるものである。即ち、本発明におけるメカノケミカル反応処理

においては、シリカに実質的に粉碎を伴う強力な剪断力を与えることによりメカノケミカル反応を行わせ、表面処理剤を化学的にシリカ表面に結合せしめて、シリカの粒子表面を十分に活性化するものである。このように、本発明では実質的にシリカの粉碎を伴なわしめることが必須である。特開昭62-12609号公報記載のようなシリカ形状を球状に保つべく実質的に粉碎を伴わない程度の剪断力では、表面処理剤をシリカ粒子の表面に結合することができないことが見出だされた（本明細書比較例4）。従って、これを半導体封止用エポキシ樹脂組成物に使用した場合には本発明のように十分に水の侵入を防ぐことができない。

【0013】該メカノケミカル反応処理は、シリカの活性な新鮮断面を保持するため不活性ガス雰囲気下で実施し、例えば、ドライ窒素ガス、ヘリウム中等で実施することが好ましい。また、該処理に際して、表面処理剤の添加量はシリカに対して0.1～3.0重量%、特に0.3～1.5重量%が好ましい。表面処理剤の添加量が0.1重量%未満では表面処理剤の効果が得られず、又3.0重量%を越えるとシリカが凝集を起こし使用時に問題となる。メカノケミカル反応処理に用いる装置は、通常の粉碎に使用される装置であればいかなるものであってもよく、例えば振動ボールミル、回転ボールミル等があげられる。処理時間は、使用する粉碎装置等により異なるが、好ましくは1～10時間であり、該処理においては、実質的な粉碎を伴わしめ所定の最大粒径及び平均粒径を得る。該処理において与えられる剪断力は、シリカが実質的に粉碎を伴うものであり、処理後のシリカの最大粒径が150μm以下、好ましくは75μm以下であり、また、その平均粒径は、1～100μm、好ましくは5～30μmである。最大粒径が150μmを越えると、半導体封止時に局部応力を発生し信頼性の低下を招く。また、該処理は、乾式の噴霧方式で行う。

【0014】本発明で使用されるエポキシ樹脂は通常使用されているものでよく、例えばビスフェノール型、クレゾールノボラック型のエポキシ樹脂等が挙げられる。該エポキシ樹脂は、イオン性不純物の含有量が多いと封止後の半導体の耐湿信頼性に悪影響を及ぼすため、ナトリウムイオンや塩素イオン等のイオン性不純物の含有量の極力少ないものが好ましい。

【0015】また、本発明で使用される硬化剤も通常使用されているものでよく、多価フェノール類、芳香族系多塩基酸類、芳香族ポリアミン類等が挙げられ、例えばフェノールノボラック、ビフェノール型ノボラック、ビスフェノールA型ノボラック等のノボラック、無水タル酸、無水ピロメリット酸、無水ベンゾフェノンテトラカルボン酸等の酸無水物あるいはジアミノジフェニルメタン、ジアミノジフェニルスルホン、メタフェニレンジアミン等のアミン等が使用される。

【0016】表面改質シリカの配合量は、上記のエポキシ樹脂及び硬化剤100重量部に対して100～800重量部、好ましくは200～600重量部である。該表面改質シリカの配合量が100重量部未満では、硬化したエポキシ樹脂組成物の線膨脹係数及び吸水率が高くなり、封止した半導体の耐湿性が悪くなる。また、配合量が800重量部を越えると、エポキシ樹脂組成物の粘度が上昇し封止作業性が悪くなる。

【0017】本発明のエポキシ樹脂組成物は、以上述べた成分の他に、必要に応じて通常使用される種々の添加剤、例えば第三級アミン類や有機リン化合物等の硬化触媒、又は難燃材、着色剤、離型剤等を配合することができる。

【0018】本発明のエポキシ樹脂組成物の調製は、以上述べた成分を、例えばニーダー、ロール、ミキサー等により混練することにより行うことができる。

【0019】本発明の表面改質シリカを含むエポキシ樹脂組成物を用いると、該表面改質シリカがエポキシ樹脂と反応もしくは相溶することによりシリカ界面に隙間のない半導体プラスチック封止が可能となる。耐湿性、特に半田後の耐湿性に優れるエポキシ樹脂封止により、IC、特にコンパクト電子機器（ノート型パソコン、VTR等）に搭載される表面実装型ICの寿命を高めることが可能となる。

【0020】このように本発明は、信頼性の面で特に問題となるシリカと樹脂の界面の隙間を飛躍的に減少させたエポキシ樹脂組成物であり、エポキシ樹脂と反応する官能基もしくは相溶する基を持つ表面処理剤をメカノケミカル反応処理により化学的に結合させた表面改質シリカを含むことを特徴とするものである。

【0021】以下、実施例、比較例により本発明を更に詳しく説明するが、本発明はこれらの実施例に限定されるものではない。尚、以下の実施例、比較例中で部とあるのは全て重量部を示し、また%は重量%を示す。

【0022】

【実施例】

【0023】

【実施例1】 (A) メカノケミカル反応処理

結晶シリカ（平均粒径2mm）71部と表面処理剤としてγ-グリシドキシプロピルトリメトキシシラン（日本ユニカ（株）商品名A-187）1部をドライ窒素ガス雰囲気中で回転ボールミルを使用して3時間粉碎してメカノケミカル反応処理を施し、平均粒径5μmの表面改質シリカを製造した。

【0024】表面改質シリカをTHFで洗浄して化学的に結合していない表面処理剤を除去した後に、元素分析で炭素量を定量すること（C:0.22%）及びFT-IRで官能基分析を実施し、メカノケミカル反応処理によりシリカに表面処理剤が反応したことを確認した。

【0025】 (B) 樹脂組成物の製造

上記処理により得られた表面改質シリカ72部、クレゾールノボラックエポキシ樹脂(EOCN-4400、日本化薬社製)15部、硬化剤としてのフェノールノボラック8部、トリフェニルホスフィン0.2部、臭素化エポキシ樹脂2部、三酸化アンチモン2部、カーボンブラック0.3部、離型剤0.5部をレーディグミキサーで混合後、二本ロールを使用し85~95℃で5分間混練しエポキシ樹脂組成物を調製した。得られたエポキシ樹脂組成物についてシリカ界面の隙間、耐湿性及び半田後耐湿性を評価した。その結果を表1に示す。

## 【0026】

## 【実施例2】(A)メカノケミカル反応処理

熔融シリカ(平均粒径30μm)71部と表面処理剤としてβ-(3,4-エポキシシクロヘキシル)エチルトリメトキシシラン(日本ユニカ(株)商品名A-186)1部をドライ窒素ガス雰囲気中で振動ボールミルを使用して5時間粉碎し、平均粒径10μmの表面改質シリカを製造した。

【0027】 続いて、実施例1と同様にして、シリカに表面処理剤が反応したことを確認した。元素分析の結果、炭素量は0.38%であった。FT-IRスペクトルチャートは図1に示す。Si-OH及びC-Hに基づく吸収が認められる。

## 【0028】(B)樹脂組成物の製造

上記の表面改質シリカを使用した以外は実施例1(B)と同様にしてエポキシ樹脂組成物を調製し、各特性を評価した。その結果を表1に示す。

## 【0029】

## 【実施例3~5】(A)メカノケミカル反応処理

実施例1(A)において表面処理剤として使用したγ-グリシドキシプロピルトリメトキシシランをそれぞれジフェニルジメトキシシラン、ステレン、MMAにかえた以外は実施例1(A)と同様にして表面改質シリカを製造し、シリカに表面処理剤が反応したことを確認した。

## 【0030】(B)樹脂組成物の製造

上記のそれぞれの表面改質シリカを使用した以外は実施例1(B)と同様にしてエポキシ樹脂組成物を調製し、各特性を評価した。その結果を表1に示す。

【0031】以上、実施例で示すようにシリカ表面に十分に表面処理剤を結合させることができ、硬化後のエポキシ樹脂組成物はシリカ界面の隙間もなく、耐湿性、半田後耐湿性に優れていることが認められた。

## 【0032】

【比較例1】結晶シリカにメカノケミカル反応処理を施さず、下記のように実施例1と同様の配合で樹脂組成物を製造した。

\*

表1

実施 例	シリカ		処理剤		評価		
	種類	重量 部	種類	重量 部	界面 隙間	耐湿性	半田後 耐湿性

\*【0033】結晶シリカ(平均粒径15μm)71部、表面処理剤としてγ-グリシドキシプロピルトリメトキシシラン(日本ユニカ(株)商品名A-187)1部、クレゾールノボラックエポキシ樹脂(EOCN-4400、日本化薬社製)15部、硬化剤としてのフェノールノボラック8部、トリフェニルホスフィン0.2部、臭素化エポキシ樹脂2部、三酸化アンチモン2部、カーボンブラック0.3部、離型剤0.5部を使用して実施例1(B)と同様にしてエポキシ樹脂組成物を調製し、各特性を評価した。その結果を表1に示す。

## 【0034】

【比較例2、3】シリカとして熔融シリカ(平均粒径10μm)、表面処理剤としてβ-(3,4-エポキシシクロヘキシル)エチルトリメトキシシラン(日本ユニカ(株)商品名A-186)又はMMAを使用した以外は比較例1と同様にしてエポキシ樹脂組成物を調製し、各特性を評価した。その結果を表1に示す。

【0035】以上、比較例1、2、3に示されるように、メカノケミカル反応処理を施さず調製した硬化後のエポキシ樹脂組成物は、シリカ界面に隙間を有し、耐湿性、半田後耐湿性は不良であった。

## 【0036】

【比較例4】熔融球状シリカ(平均粒径10μm)71部に表面処理剤としてγ-グリシドキシプロピルトリメトキシシラン(日本ユニカ(株)商品名A-187)1部をドライ窒素ガス雰囲気中で回転ボールミルを使用して10時間、実質的に粉碎が生じないようにしてメカノケミカル反応処理を施した。

【0037】得られたシリカについて、実施例1と同様に元素分析によって炭素量を定量した。その結果、炭素量は検出限界の0.05%以下であり、表面処理剤がシリカに化学的に結合していないことが判明した。また、比較例4のFT-IRスペクトルチャートを図2に示す。Si-OH及びC-Hに基づく吸収は認められない。比較例4の結果から、粉碎を生じないメカノケミカル反応処理ではシリカ表面に殆ど表面処理剤を結合することができないことが認められた。

【0038】得られたシリカから実施例1(B)と同様にしてエポキシ樹脂組成物を調製し、各特性を評価した。その結果を表1に示す。硬化したエポキシ樹脂組成物はシリカ界面に隙間を有し、耐湿性、半田後耐湿性は実施例1の硬化したエポキシ樹脂組成物と比較して、著しく劣っていた。

## 【0039】

## 【表1】

1	結晶 シリカ	71	A- 187	1	メカノケ ミカル法	なし	0/20	2/20
2	熔融 シリカ	"	A- 186	"	"	"	0/20	0/20
3	"	"	ジフェニル ジメトキシ シラン	"	"	"	0/20	1/20
4	"	"	スチレン	"	"	"	1/20	3/20
5	"	"	MMA	"	"	"	1/20	5/20
比較 例								
1	結晶 シリカ	71	A- 187	1	従来法	あり	2/20	20/20
2	熔融 シリカ	"	A- 186	"	"	"	2/20	16/20
3	"	"	MMA	"	"	"	4/20	20/20
4	熔融球 状シリ カ	"	A- 187	"	メカノケ ミカル法 (粉碎なし)	"	5/20	15/20

表1中の評価方法は下記の通りである。

【0040】界面隙間：各々の樹脂組成物で曲げテストピースを作成し、これを125℃、湿度100%条件下で20時間吸湿させた後、破断する。この破断面をSEMで観察し、シリカ界面の0.1mm以上の隙間の有無で判断した。

【0041】耐湿性：アルミ模擬素子を封止した16pin SOPを125℃、湿度100%条件下100時間放置後のリーク不良数/テスト数で示した。

【0042】半田後耐湿性：アルミ模擬素子を封止した16pin SOPを85℃、湿度85%条件下168時間吸湿させた後、260℃の半田浴に10秒間浸漬させる。その後、125℃、湿度100%条件下で500\*

\*時間放置した後のオープン不良数/テスト数で示した。

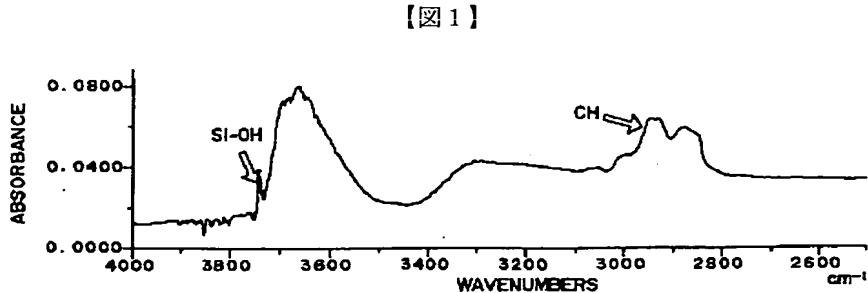
#### 【0043】

【発明の効果】以上のように本発明の半導体封止用エポキシ樹脂組成物は、シリカ界面に隙間のない半導体プラスチック封止を可能とする。また、耐湿性、半田後耐湿性に優れるエポキシ樹脂封止により、表面実装型ICの寿命を高めることが可能となる。

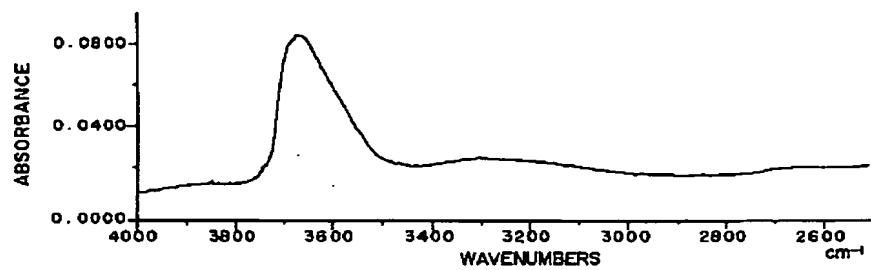
#### 【図面の簡単な説明】

【図1】実施例2のメカノケミカル反応処理により製造した表面改質シリカのFT-IRスペクトルである。

【図2】比較例4の実質的に粉碎を伴わないメカノケミカル反応処理により製造したシリカのFT-IRスペクトルである。



【図2】



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## (54) METHOD OF MANUFACTURING SURFACE MODIFIED SPHERICAL INORGANIC POWDER

### (57)Abstract:

**PROBLEM TO BE SOLVED:** To easily provide a spherical inorganic powder treated with a proper quantity of silane coupling agent without causing break of the spherical inorganic powder, preventing generation of coagulated particles, and without contaminating foreign matters, especially, the one treated with the silane coupling agent and having a surface OH group density of not higher than 3.0 OH groups/nm<sup>2</sup>, and suitable as a filler for a resin composition for semiconductor sealing excellent in fluidity, moisture absorption, and adhesion property.

**SOLUTION:** In this method of manufacturing a surface modified spherical inorganic powder, a silane coupling agent solution is sprayed making the diameter of the liquid particle not greater than 200 µm, while stirring the spherical inorganic powder having an average sphericity of not lower than 0.70 and giving it a shearing force of a degree not causing it to break.

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最終頁に続く

(54)【発明の名称】 表面改質球状無機質粉末の製造方法

(57)【要約】

【課題】球状無機質粉末の破壊を起こさせず、また凝集粒子の発生を抑制し、かつ異物を混入させることなく、適切量のシランカップリング剤で処理された球状無機質粉末を容易に製造すること。特に、流動性、吸湿性、密着性に優れる半導体封止用樹脂組成物の充填材として好適な、シランカップリング剤で処理された表面OH基密度3.0個/nm<sup>2</sup>以下の球状シリカ粉末を容易に製造すること。

【解決手段】平均球形度が0.70以上の球状無機質粉末に、その破壊を起こさせない程度のせん断力を与えて攪拌をしながら、シランカップリング剤液をその液滴径200μm以下にして噴霧することを特徴とする表面改質球状無機質粉末の製造方法。

## 【特許請求の範囲】

【請求項1】 平均球形度が0.70以上の球状無機質粉末に、その破壊を起こさせない程度のせん断力を与えて攪拌をしながら、シランカップリング剤液をその液滴径200μm以下にして噴霧することを特徴とする表面改質球状無機質粉末の製造方法。

## 【発明の詳細な説明】

## 【0001】

【発明の属する技術分野】 本発明は、シランカップリング剤により表面改質された球状無機質粉末の製造方法に関する。

## 【0002】

【従来の技術】 従来、半導体封止用樹脂組成物においては、その熱膨張係数をSiチップに近づけ、またマトリックス樹脂分の相対量を減じて低吸湿化を実現させるために、球状シリカ粉末、球状アルミナ粉末等の球状無機質粉末が使用されている。

【0003】 球状無機質粉末は、その表面形状が平滑であるので、マトリックス樹脂との結合が弱く、曲げ強度等の機械的特性が破碎状無機質粉末よりも小さくなる。そこで、これを改善するため、シリカ質粉末の表面をシランカップリング剤で処理することが行われている（例えば、特開平5-335446号公報）。

【0004】 しかしながら、シランカップリング剤の液滴がシリカ粉末に局所的に添加されると凝集粒子を生じ、これが半導体樹脂組成物中に混合され成形されると、凝集粒子に起因するボイドが生じ曲げ強度等が十分に高まらず、均一処理を施すのに特別な配慮が必要となる。また、必要量以上のシランカップリング剤の使用は、カップリング剤がシリカ表面の孤立Si-OHと反応せず物理吸着されるため、著しい流動性の低下及び曲げ強度の低下の原因となる。更には、上記先行技術は、高い攪拌力を用いるメカノケミカル反応を利用するものであるため、処理中に球状シリカが破壊され、球状シリカの利点である樹脂に充填した際の高充填性、高流動性が著しく損なわれることから、球状シリカ粉末の処理には不向きである。

【0005】 一方、メカノケミカル反応を利用しないで球状シリカ粉末をシランカップリング剤で処理することも知られている（特開昭62-12609号公報）が、均一な表面改質を行うには長時間を要するため、生産性の低下、粉碎機の壁材や分散媒体からの異物の混入が問題となる。また、均一な処理効果についても、十分に満足することができなかった。

【0006】 そこで、今日の課題は、破壊を起こさせず、また凝集粒子の発生を抑制し、かつ異物も混入させることなく、適切量のシランカップリング剤で球状無機質粉末の表面を容易かつ均一に処理することである。

## 【0007】

【発明が解決しようとする課題】 本発明は、流動性、吸

湿性、密着性に優れる半導体封止用樹脂組成物の充填剤として好適な、シランカップリング剤で処理された表面OH基密度3.0個/nm<sup>2</sup>以下の球状シリカ粉末を、球状無機質粉末の破壊を起こさせず、また凝集粒子の発生を抑制し、かつ異物を混入させることなく、適切量のシランカップリング剤の処理によって容易に製造する方法を提供することである。

## 【0008】

【課題を解決するための手段】 すなわち、本発明は、平均球形度が0.70以上の球状無機質粉末を、その破壊を起こさせない程度のせん断力を与えて攪拌をしながら、シランカップリング剤液をその液滴径200μm以下にして噴霧することを特徴とする表面改質球状無機質粉末の製造方法である。

## 【0009】

【発明の実施の形態】 以下、更に詳しく本発明について説明する。

【0010】 本発明で使用されるシランカップリング剤としては、ビニルトリクロルシラン、ビニルトリエトキシシラン、ビニルトリメトキシシラン、γ-メタクリロキシプロピルトリメトキシシラン、β-(3,4エポキシシンクロヘキシル)エチルトリメトキシシラン、γ-グリシドキシプロピルトリメトキシシラン、γ-グリシドキシプロピルメチルジエトキシシラン、N-β-(アミノエチル)γ-アミノプロピルトリメトキシシラン、N-β-(アミノエチル)γ-アミノプロピルメチルジメトキシシラン、γ-アミノプロピルトリエトキシシラン、N-フェニル-γ-アミノプロピルトリメトキシシラン、γ-メルカプトプロピルトリメトキシシラン、γ-クロロプロピルトリメトキシシラン等が使用可能であり、これらを単独、又は二種類以上混合して用いることができる。

【0011】 また、本発明が対象としている球状無機質粉末は、球状シリカ、球状アルミナ、球状ムライト、球状窒化アルミニウム等の材質であって、その粉末の平均球形度が0.70以上のものである。平均球形度が0.70未満であると、樹脂組成物に高充填することができなくなり、特に耐吸湿性が低下する。また、樹脂組成物の成形性が悪化する

【0012】 ここで平均球形度は、次のように求められる。粒子像解析装置（例えば、Sysmex社製「FP-IA-1000」）を用い、1000個以上の粒子像それぞれの投影面積(A)と周囲長(PM)を測定する。周囲長(PM)に対応する真円の半径をrとすると、 $PM = 2\pi r$ であることから、 $r = PM / 2\pi$ となる。先に仮定した真円の面積を(B)とすると、 $B = (PM)^2 / 4\pi$ となる。ここで粒子の球形度は $A/B$ として計算されるので、個々の粒子の球形度は、式、球形度 $= A/B = A \times 4\pi / (PM)^2$ 、として算出することができる。よって、平均球形度は、平均球形度 $= (\Sigma \text{球形度}) / \text{粒子数}$

度)  $/ n$  ( $n \geq 1000$ )、として算出することができる。

【0013】本発明において、上記球状無機質粉末を上記シランカップリング剤で処理するには、球状無機質粉末を振動ミル又はボールミル等の攪拌装置に投入し、球状シリカ粉末の破壊が起らぬ程度のせん断力を付与して攪拌しながら、シランカップリング剤を流体ノズル等のノズルから噴霧することによって行われる。

【0014】本発明で重要なことは、シランカップリング剤を液滴径  $200 \mu\text{m}$  以下、好ましくは  $100 \mu\text{m}$  以下にして噴霧することである。液滴径がこれよりも大きいと、シランカップリング剤が球状無機質粉末に局所的に添加されるため、凝集粒子量が著しく増加する。

【0015】また、シランカップリング剤を流体ノズルを用いて噴霧し攪拌する際のせん断力は、球状無機質粉末の破壊が起らぬ程度の力であり、好ましくは破壊係数が  $0.10$  以下 ( $0$  を含む)、特に  $0.08$  以下 ( $0$  を含む) にして攪拌することである。破壊係数が  $0.10$  を超えると球状シリカ粉末の利点である流動性及び高充填性が損なわれる。

【0016】ここでいう破壊係数とは、式、破壊係数 =  $(|\text{原料粉末の平均球形度} - \text{表面改質粉末の平均球形度}|) / \text{原料粉末の平均球形度}$ 、として算出される。例えば、平均球形度が  $0.80$  である球状シリカ粉末原料を表面改質して得られた表面改質球状無機質粉末の平均球形度が  $0.79$  であれば、上式に従って、破壊係数は  $0.01$  と算出される。

【0017】攪拌時間は  $20 \sim 120$  分が望ましく、 $20$  分よりも短いと、球状無機質粉末原料とシランカップリング剤とが十分に反応することができず、均一な表面改質処理が困難となる。一方、カップリング反応は  $120$  分以内で終了するため、 $120$  分を超える攪拌は壁材及び分散媒体からの異物の混入が増加することに加えて、表面改質に長時間を要することになるので生産性が低下する。

【0018】攪拌時間は改質処理される球状無機質粉末原料の種類、粒度、シランカップリング剤の種類に応じて、上記の範囲内で適宜決定される。

【0019】表面改質処理の系内温度は、シランカップリング剤の種類に応じ、それが熱分解をしない温度領域で適宜決定される。例えば、シランカップリング剤が  $\gamma$ -アミノプロピルトリエトキシシランである場合の系内温度は、 $20 \sim 180^\circ\text{C}$  であり、望ましくは  $80 \sim 150^\circ\text{C}$  である。

【0020】本発明の表面改質方法は、特に、流動性、吸湿性、密着性に優れる半導体封止用樹脂組成物の充填材として好適な、シランカップリング剤で処理された球状シリカ粉末を破壊を起させず、また凝集粒子の発生を抑制し、かつ異物も混入させることなく製造するのに適用される。

【0021】その際のシランカップリング剤の使用量は、球状シリカ粉末の表面OH基密度が  $3.0 \text{ 個} / \text{nm}^2$  以下、特に  $2.0 \text{ 個} / \text{nm}^2$  以下となる量であることが好ましい。表面OH基密度が  $3.0 \text{ 個} / \text{nm}^2$  よりも大きくなると、表面OH基と反応する水分量が増えるため、半導体封止用樹脂組成物の吸湿性が悪化し、はんだ処理時のパッケージクラック等の発生を招く。また、表面の孤立  $\text{Si}-\text{OH}$  とシランカップリング剤とが反応していない未反応部位が多くなり、球状シリカ粉末とマトリックス樹脂との密着性が損なわれ、曲げ強度等が低下する。

【0022】本発明においては、表面OH基密度が  $3.0 \text{ 個} / \text{nm}^2$  以下にあっても、以下で測定された凝集粒子増加率が  $2.0$  以下であることが特に好ましい。これによって、半導体封止用樹脂組成物として用いても凝集粒子量が少ないため、それに起因するボイドが生じにくくなり、成形品の曲げ強度の低下を著しく防止することができる。

【0023】ここでいう凝集粒子増加率とは、式、凝集粒子増加化率 = 表面改質粉末の凝集粒子量 / 原料粉末の凝集粒子量、として算出される。例えば、平均粒径  $17.6 \mu\text{m}$ 、比表面積  $5.85 \text{ m}^2 / \text{g}$  の球状シリカ粉末原料を表面改質処理した際は、原料粉末及び表面改質粉末をそれぞれ目開き  $75 \mu\text{m}$  の篩を用いて篩い分けし、篩残分を凝集粒子とみなし、両者の比を上式に従って算出する。

#### 【0024】

【実施例】以下、実施例及び比較例をあげて本発明を更に具体的に説明する。

#### 【0025】実施例1～6 比較例1～4

原料球状シリカ粉末 (平均粒径  $17.6 \mu\text{m}$ 、 $50.0 \mu\text{m}$ )  $20.0 \text{ kg}$  を振動ボールミルに入れ、その破壊係数が  $0.10$  以下になるようなせん断力を与えながら攪拌し、 $\gamma$ -アミノプロピルトリエトキシシラン  $0.13 \text{ kg}$  を、液滴径を変えて流体ノズルから噴霧した。攪拌時間は  $60$  分とした。原料球状シリカ粉末及び表面改質球状シリカ粉末の粉体特性を表1に示す。

#### 【0026】

#### 【表1】

に対し、比較例1～4のように液滴径が200μmを超えると、表面改質球状シリカ粉末のそれらの値が著しく異なったものになることから、平均球形度を維持するためにも液滴径を200μm以下とすることが望ましい。

【0030】次に、上記実施例、比較例で得られた表面改質球状シリカ粉末の半導体封止用樹脂組成物への充填材としての特性を評価するため、質量基準で、表面改質球状シリカ粉末85部、オルトクレゾールノボラック型エポキシ樹脂8、9部、フェノールノボラック樹脂4、

1部、トリフェニルホスフィン0、4部、カルナバワックス1、3部、カーボンブラック0、3部をミキサーにてドライブレンドした後、100℃でロール混練し、冷却後、粉碎して得られたエポキシ樹脂組成物について、以下に従う流動性（スパイラルフロー値）、曲げ強度、はんだ耐熱性（クラック発生率）を測定した。それらの結果を表2に示す。

【0031】

【表2】

噴霧液滴径 (μm)	実施例1		実施例2		実施例3		実施例4		実施例5		実施例6		比較例1		比較例2		比較例3		比較例4	
	50	100	200	50	100	200	500	1000	200	500	1000	500	1000	500	1000	500	1000	500	1000	
原料球状シリカ粉末	17.6	17.6	17.6	5.85	5.85	5.85	0.60	0.60	0.60	5.85	5.85	0.60	0.60	0.60	0.60	0.60	0.60	0.60	0.60	
比表面積 (m <sup>2</sup> /g)																				
平均球形度 (-)	0.79	0.79	0.79	0.79	0.79	0.79	0.85	0.85	0.85	0.85	0.85	0.79	0.79	0.79	0.79	0.79	0.79	0.79	0.79	
OH基密度 (個/nm <sup>2</sup> )	7.2	7.2	7.2	7.2	7.2	7.2	5.3	5.3	5.3	5.3	5.3	7.2	7.2	7.2	7.2	7.2	7.2	7.2	7.2	
表面改質球状シリカ粉末	17.5	17.4	18.2	5.92	5.94	5.88	0.62	0.60	0.61	5.79	5.66	0.60	0.60	0.60	0.60	0.60	0.60	0.60	0.60	
比表面積 (m <sup>2</sup> /g)																				
平均球形度 (-)	0.79	0.79	0.79	0.76	0.76	0.76	0.84	0.84	0.85	0.81	0.81	0.70	0.70	0.70	0.70	0.70	0.70	0.70	0.70	
OH基密度 (個/nm <sup>2</sup> )	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	
凝集粒子增加率 (-)	1.12	1.16	1.24	1.01	1.01	1.05	1.05	1.05	1.05	1.05	1.05	2.51	2.51	2.51	2.51	2.51	2.51	2.51	2.51	

【0027】表1から明らかなように、表面OH基密度が3.0個/nm<sup>2</sup>である表面改質球状シリカ粉末を得るために、実施例1～6のようにシランカップリング剤の液滴径を200μm以下にする必要があることがわかる。

【0028】また、凝集粒子增加率を2.0以下にするためにも、実施例1～6のように液滴径を200μm以下にして噴霧する必要がある。これを、比較例1～4のように液滴径が200μmを超えると、凝集粒子增加率が2.0をこえてしまう。

【0029】更には、表面改質球状シリカ粉末の平均球形度を0.70以上とするためには、必ずしも液滴径が200μm以下とする必要はない。しかし、実施例1～6のように、液滴径を200μm以下にして噴霧すると、表面改質球状シリカ粉末の平均球形度、平均粒径、比表面積がその原料球状シリカ粉末とほぼ等しくなるの

7						
表面改質球状シリカ粉末の種類	実施例1	実施例2	実施例3	実施例4	実施例5	実施例6
スパイラルフロー値 (cm)	94	90	75	75	74	75
曲げ強度 (MPa)	161	160	132	135	137	146
クラック発生率 (%)	0	0	0	0	0	6
破壊係数 (-)	0.00	0.04	0.01	0.00	0.05	0.11

【0032】表2から、実施例1～6で得られた表面改質球状シリカ粉末のように、平均球形度が0.70以上で、かつ凝集粒子増加率が少なく、しかも破壊係数が0.10以下となるようなせん断力を与えて表面改質されたものを使用すると、そうでない比較例1～4に比べて、樹脂組成物の流動性が高まり、得られた樹脂成形品の曲げ強度が高く、クラック発生率が著しく小さくなる\*

\*ことがわかる。

【0033】なお、実施例及び比較例における各物性は次のように測定した。

【0034】(1) 表面OH基密度

表面改質球状シリカ粉末を250°Cにて加熱し物理吸着水を除去した後、カールフィッシュレー微量水分測定器（例えば三菱化学社製「CA-05型」）にてOH基量を測定した。

【0035】(2) 凝集粒子増加率

10 上記に測定した。使用した篩は、測定する球状シリカ粉末の平均粒径により次のように決定した。平均粒径が0.1～5μmの球状シリカ粉末では目開き25μmの篩、平均粒径5～30μmのものでは目開き75μmの篩、平均粒径40～60μmのものでは目開き150μmの篩を用いた。

【0036】(3) 流動性（スパイラルフロー値）

スパイラルフロー金型を用い、EMMI-66に準拠してスパイラルフローを測定した。成形温度は175°C、成形圧力は7.4MPaで行った。

20 【0037】(4) 曲げ強度

樹脂組成物を金型温度180°Cで、4mm×16mm×80mmの大きさに成形し、180°C×6時間で硬化を行った後、JIS K 6911の曲げ強度の測定法に準拠して行った。

【0038】(5) はんだ耐熱性（クラック発生率）

低圧トランスマルチ成形法により175°C×2分の条件で模擬素子を封止した44ピンQFP成形体（パッケージ）を16個得、175°C×5時間のポストキュアを行った。これらを温度85°C、湿度85RH%の条件下に

30 96時間放置後、260°Cのはんだに10秒間浸漬し超音波探査映像装置により、16個の成形体中に観察された内部クラックの発生率を求めた。

【0039】

【発明の効果】本発明によれば、球状無機質粉末の破壊を起こさせず、また凝集粒子の発生を抑制し、かつ異物を混入させることなく、適切量のシランカップリング剤で処理された球状無機質粉末を容易に製造することができる。特に、流動性、吸湿性、密着性に優れる半導体封止用樹脂組成物の充填材として好適な、シランカップリング剤で処理された表面OH基密度3.0個/nm<sup>2</sup>以下の球状シリカ粉末を容易に製造することができる。

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## (54) INORGANIC POWDER AND RESIN COMPOSITION FILLED THEREWITH

(57)Abstract:

**PROBLEM TO BE SOLVED:** To provide a resin composition which has high heat conductivity, high flowability, low mold wearability and is useful for sealing materials and so on, and to provide inorganic powder suitable for producing the resin composition.

**SOLUTION:** This inorganic powder characterized by comprising spherical silica powder having an average particle diameter of  $\leq 1.0 \mu\text{m}$  and an average spherical degree of  $\geq 0.90$  and spherical alumina powder having an average spherical degree of  $\geq 0.85$  and consisting mainly of particles having particle diameters in the range of 1 to  $96 \mu\text{m}$ , wherein the content of the spherical silica powder is 3 to 30%. And the resin composition characterized by containing the inorganic powder.

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(54)【発明の名称】 無機質粉末及びそれが充填された樹脂組成物

(57)【要約】

【課題】高熱伝導性・高流動性・低金型摩耗性を有する封止材等の樹脂組成物と、その製造に好適な無機質粉末を提供すること。

【解決手段】平均粒子径1.0μm以下で、その平均球形度が0.90以上である球状シリカ粉末と、粒子径範囲1~9.6μmの粒子を主体とし、その平均球形度が0.85以上である球状アルミナ粉末とを含み、球状シリカ粉末の含有率が3~30%の混合粉末からなることを特徴とする無機質粉末。及びこの無機質粉末を含有してなることを特徴とする樹脂組成物。

## 【特許請求の範囲】

【請求項1】 平均粒子径1.0μm以下で、その平均球形度が0.90以上である球状シリカ粉末と、粒子径範囲1～96μmの粒子を主体とし、その平均球形度が0.85以上である球状アルミナ粉末とを含み、球状シリカ粉末の含有率が3～30%の混合粉末からなることを特徴とする無機質粉末。

【請求項2】 請求項1記載の無機質粉末を含有してなることを特徴とする樹脂組成物。

## 【発明の詳細な説明】

## 【0001】

【発明の属する技術分野】 本発明は、無機質粉末及びそれが充填された樹脂組成物に関するものであり、電子・電気機器等の絶縁封止材、各種基板の製造に好適なものである。

## 【0002】

【従来の技術】 近年、ICの高機能化及び高速化の進展に伴い、その発熱量は増大傾向にある。これを受け、封止材に対しても高熱放散性の要求が高まっており、それを構成するエポキシ樹脂とフィラーの両面から検討が進められている。従来、高熱伝導性フィラーとしては、窒化アルミニウム、窒化ケイ素及び酸化アルミニウム（アルミナ）が主として使用されているが、これらには一長一短がある。

【0003】 窒化アルミニウム、窒化ケイ素は、それ自身が100W/m·K以上の高い熱伝導性を有することから、封止材の高熱伝導化が可能な反面、非球状かつ非酸化物であることから、封止材の流動性が低下する、成型時の金型摩耗性が激しい、空気中の水分と反応してアンモニアを発生する、等の問題が懸念され、本格的に普及されるまでには至っていない。

【0004】 これに対し、アルミナは水分と反応しないのでアンモニア発生の心配はないが、流動性と金型摩耗性については、上記窒化物と同等レベルであり、まだ改善の余地があった。そこで、特開平5-294613号公報、特開平11-147711号公報のように、アルミナ粒子を球状化して用いる提案がなされているが、まだ十分ではなく、高熱伝導性と共に高流動性・低金型摩耗性を有する封止材の開発が待たれていた。

## 【0005】

【発明が解決しようとする課題】 本発明は上記に鑑みてなされたものであり、その目的は、高熱伝導性・高流動性・低金型摩耗性を有する封止材等の樹脂組成物と、それに用いられる無機質粉末を提供することである。

## 【0006】

【課題を解決するための手段】 すなわち、本発明は、平均粒子径1.0μm以下で、その平均球形度が0.90以上である球状シリカ粉末と、粒子径範囲1～96μmの粒子を主体とし、その平均球形度が0.85以上である球状アルミナ粉末とを含み、球状シリカ粉末の含有率

が3～30%の混合粉末からなることを特徴とする無機質粉末である。また、本発明は、この無機質粉末を含有してなることを特徴とする樹脂組成物である。

## 【0007】

【発明の実施の形態】 以下、更に詳しく本発明について説明する。

【0008】 本発明の無機質粉末は、球状アルミナ粉末と、その球状アルミナ粉末よりも微粒かつ平均球形度の大きい球状シリカ粉末とから構成されている。このようにする理由は、アルミナ自身の熱伝導率は、30W/m·K程度と上記窒化物に比べて小さいが、その充填量を樹脂組成物（以下、樹脂組成物と封止材を特に区別する必要がないときには、「封止材」ともいう。）の高流動性と低金型摩耗性を損なわせない範囲で可及的に高め、封止材の高熱伝導化を実現させるためである。

【0009】 本発明で使用される球状アルミナ粉末は、粒子径範囲1～96μmの粒子を主体とし、その平均球形度が0.85以上のものである。球状アルミナ粉末は、主として封止材への高熱伝導付与材として機能させるものであるが、封止材の高流動性・低金型摩耗性を損なわせないために、上記粒子径範囲と平均球形度にする必要がある。

【0010】 球状アルミナ粉末に96μm超の粒子が多量に含まれていると、流動性が低下し、また成型時の金型摩耗量が増大する。本発明においては、96μm超の粒子は皆無であることが好ましい。また、1μm未満の粒子も高流動性を発現させるためにできるだけ存在させない方が好ましいが、3%程度量までは許容できる。

【0011】 また、球状アルミナ粉末の平均球形度が0.85未満では、封止材の流動性が低下し、金型摩耗量が増大する。好ましい平均球形度は0.90以上である。

【0012】 本発明で使用される球状シリカ粉末は、主として封止材の高流動化及び低金型摩耗化として機能するものであり、シリカ質以外の超微粉ではこの効果を十分に発現させることは困難である。

【0013】 本発明においては、球状シリカ粉末の平均粒子径が1.0μmをこえると封止材の流動性が低下する。また、平均球形度が0.90未満であっても封止材の流動性が損なわれ、金型摩耗量が増大するようになる。特に好ましい平均球形度は0.95以上であり、上記球状アルミナ粉末よりも大きいことである。特に好ましい平均粒子径は0.2～0.8μmである。

【0014】 球状アルミナ粉末と球状シリカ粉末の構成比率については、本発明の無機質粉末中、球状シリカ粉末の含有率が3～30%、残部が実質的に球状アルミナ粉末であることが好ましい。球状シリカ粉末の含有率が30%超では封止材の熱伝導性が低下し、3%未満では高流動性が損なわれる。

【0015】 本発明の樹脂組成物の用途が、封止材であ

るときは、実質的に上記球状アルミナ粉末と上記球状シリカ粉末とで構成された無機質粉末が好適であるが、封止材以外の用途、例えばICやLSIなどの発熱部品の冷却用として用いられる放熱部材においては、柔軟性を発現させるために更にBN粉末等を含有させることができること。

【0016】本発明における粉末の粒子径は、レーザー回折式粒度分布測定機を用いて測定することができる。球状アルミナ粉末の測定には、例えばシーラスグラニュロメーター「モデル920」を、また球状シリカ粉末には、例えばコールター社製レーザー回折散乱法粒度分布測定装置「LS-230」が使用される。

【0017】また、平均球形度は、粒子の投影像により粒子形状を分析し、投影面積と粒子の投影周囲長と同じ円周を持つ円の面積との比を用いて、以下の手順によって測定することができる。

【0018】走査型電子顕微鏡（例えば日本電子社製「JSM-T200型」）と画像解析装置（例えば日本アビオニクス社製）を用い、電子顕微鏡で得られたSEM写真の画像解析を行って測定する。測定粒子数は100個以上とする。

【0019】まず、粒子の投影面積（A）と周囲長（PM）を測定する。周囲長（PM）に対応する真円の面積を（B）とすると、その粒子の真円度はA/Bとなる。そこで、試料粒子の周囲長（PM）と同一の周囲長を持つ真円を想定すると、 $PM = 2\pi r$ 、 $B = \pi r^2$ であるから、 $B = \pi \times (PM/2\pi)^2$ となり、個々の粒子の真円度は、 $A/B = A \times 4\pi / (PM)^2$ として算出する。このようにして得られた100個以上の粒子の真円度を求めて平均値を平均球形度とする。

【0020】本発明の無機質粉末は、既存の溶射技術（例えば「製鋼窯炉に対する溶射捕集技術について」製鉄研究1982第310号）を基本とし、水素、天然ガス、アセチレンガス、プロパンガス、ブタン等の燃料ガスと、酸素等の助燃ガスとで形成された高温火炎中に原料粉末を投入し、熱分解、溶融球状化させて球状アルミナ粉末と球状シリカ粉末とをそれぞれ製造し、それらを混合することによって製造することができる。

【0021】本発明で使用される球状アルミナ粉末又は球状シリカ粉末の製造工程概略図の一例を図1に示した。図1は、高温火炎の形成ないしは高温火炎の形成と共に原料粉末を高温火炎中に噴射することのできるバーナー2が設置された溶融炉1と、溶融処理物の捕集系である重力沈降室6、サイクロン7、バグフィルター8とから構成されている。なお、3は燃料ガス供給管、4は助燃ガス供給管、5は原料粉末供給管、9はプロワーである。所定の製品粉末は、捕集系内のオンライン分級、又は捕集物のオフライン分級で得ることができる。

【0022】球状アルミナ粉末製造用原料としては、水酸化アルミニウム粉末が好適である。その原料粒度は製

品粒度に概ね反映するので、予め原料粒度を製品粒度に調整しておくことが望ましいが、球状化処理後に分級処理して粒度調整を行ってもよい。水酸化アルミニウム粉末の高温火炎中への供給は、乾式又は水等でスラリー化した湿式でもよいが、製品の平均球形度は火炎温度に強く依存するので、できるだけ2000℃以上の高温火炎中に供給することが好ましい。

【0023】一方、球状シリカ粉末製造用原料としては、水晶、天然珪石等のシリカ質原料を、1μm以下の粒子割合が15～50%、5μm以上の粒子割合が50～80%の粒度構成に調整し、それを高温火炎中に供給することが好ましい。

【0024】次に、本発明の樹脂組成物について説明する。

【0025】本発明の樹脂組成物は、本発明の無機質粉末を樹脂に充填させてなるものである。充填量には特に制限がないが、樹脂組成物の用途が封止材である場合、高熱伝導性・高流動性・低金型摩耗性を実現させるために、樹脂組成物中の割合が70～75vol.%であることが好ましい。これよりも少ない充填量では、高熱伝導率の発現が困難となる一方、また多いと流動性の低下や金型摩耗量の増大につながる。

【0026】本発明で使用される樹脂としては、エポキシ樹脂、シリコーン樹脂、フェノール樹脂、メラミン樹脂、ユリア樹脂、不飽和ポリエステル、フッ素樹脂、ポリイミド、ポリアミドイミド、ポリエーテルイミド等のポリアミド、ポリブチレンテレフタレート、ポリエチレンテレフタレート等のポリエステル、ポリフェニレンスルフィド、全芳香族ポリエステル、ポリスルホン、液晶ポリマー、ポリエーテルスルホン、ポリカーボネート、マレイミド変性樹脂、ABS樹脂、AAS（アクリロニトリルーアクリルゴム・スチレン）樹脂、AES（アクリロニトリル・エチレン・プロピレン・ジエンゴムースチレン）樹脂などをあげることができる。

【0027】これらの中、封止材用樹脂としては、1分子中にエポキシ基を2個以上有するエポキシ樹脂が好ましい。その具体例をあげれば、フェノールノボラック型エポキシ樹脂、オルソクレゾールノボラック型エポキシ樹脂、フェノール類とアルデヒド類のノボラック樹脂をエポキシ化したもの、ビスフェノールA、ビスフェノールF及びビスフェノールSなどのグリシジルエーテル、フタル酸やダイマー酸などの多塩基酸とエポクロルヒドリンとの反応により得られるグリシジルエステル酸エポキシ樹脂、線状脂肪族エポキシ樹脂、脂環式エポキシ樹脂、複素環式エポキシ樹脂、アルキル変性多官能エポキシ樹脂、 $\beta$ -ナフトールノボラック型エポキシ樹脂、1,6-ジヒドロキシナフタレン型エポキシ樹脂、2,7-ジヒドロキシナフタレン型エポキシ樹脂、ビスヒドロキシビフェニル型エポキシ樹脂、更には難燃性を付与するために臭素などのハロゲンを導入したエポキシ樹脂

などである。中でも、耐湿性や耐ハンダリフロー性の点からは、オルソクレゾールノボラック型エポキシ樹脂、ビスヒドロキシビフェニル型エポキシ樹脂、ナフタレン骨格のエポキシ樹脂が好適である。

【0028】エポキシ樹脂の硬化剤については、エポキシ樹脂と反応して硬化させるものであれば特に限定されず、例えば、フェノール、クレゾール、キシレノール、レゾルシノール、クロロフェノール、*t*-ブチルフェノール、ノニルフェノール、イソプロピルフェノール、オクチルフェノール等の群から選ばれた1種又は2種以上の混合物をホルムアルデヒド、パラホルムアルデヒド又はパラキシレンとともに酸化触媒下で反応させて得られるノボラック型樹脂、ポリパラヒドロキシスチレン樹脂、ビスフェノールAやビスフェノールS等のビスフェノール化合物、ピロガロールやフロログロシノール等の3官能フェノール類、無水マレイン酸、無水フタル酸や無水ピロメリット酸等の酸無水物、メタフェニレンジアミン、ジアミノフェニルメタン、ジアミノジフェニルスルホン等の芳香族アミンなどをあげることができる。

【0029】エポキシ樹脂と硬化剤との反応を促進させるために、8-ジアザビシクロ(5,4,0)ウンデセナ-7、トリフェニルホスフィン、ベンジルジメチルアミン、2-メチルイミダゾールなどの硬化促進剤を使用することが望ましい。また、特に高い耐湿信頼性と高温放置安定性が要求される場合には、各種イオントラップ剤の添加が有効である。イオントラップ剤としては、協和化学社製商品名「DHF-4A」、「KW-2000」、「KW-2100」、東亞合成化学工業社製商品名「IXE-600」などがある。

【0030】更に、本発明の樹脂組成物には、以下の成分を必要に応じて配合することができる。すなわち、低応力化剤として、シリコーンゴム、ポリサルファイドゴム、アクリル系ゴム、ブタジエン系ゴム、スチレン系ブロックコポリマーや飽和型エラストマー等のゴム状物質、各種熱可塑性樹脂、シリコーン樹脂等や、更にはエポキシ樹脂、フェノール樹脂の一部又は全部をアミノシリコーン、エポキシシリコーン、アルコキシリコーン等で変性した樹脂などである。また、シランカップリング剤として、 $\gamma$ -グリシドキシプロピルトリメトキシシラン、 $\beta$ -(3,4-エポキシクロヘキシル)エチルトリメトキシシラン等のエポキシシラン、アミノプロピルトリエトキシシラン、ウレイドプロピルトリエトキシシラン、N-フェニルアミノプロピルトリメトキシシラン等のアミノシラン、フェニルトリメトキシシラン、メチルトリメトキシシラン、オクタデシルトリメトキシシラン等の疎水性シラン化合物やメルカプトシランなど、表面処理剤として、Zrキレート、チタネートカップリング剤、アルミニウム系カップリング剤など、難燃助剤として、Sb<sub>2</sub>O<sub>3</sub>、Sb<sub>2</sub>O<sub>4</sub>、Sb<sub>2</sub>O<sub>5</sub>など、難燃剤として、ハロゲン化エポキシ樹脂やリン化合物など、着色

剤として、カーボンブラック、酸化鉄、染料、顔料などである。更には、離型剤として、天然ワックス類、合成ワックス類、直鎖脂肪酸の金属塩、酸アミド類、エステル類、パラフィンなどを配合することができる。

【0031】本発明の樹脂組成物は、上記諸材料をブレンダーやミキサーで混合した後、加熱ロール、ニーダー、一軸又は二軸押出機、バンパリーミキサーなどによって溶融混練し、冷却後に粉碎することによって製造することができる。

10 【0032】本発明の樹脂組成物を用いて半導体素子を封止するには、トランスマーモールド、マルチプランジャーなどの成型法を採用することができる。

【0033】

【実施例】以下、実施例、比較例をあげて更に具体的に本発明を説明する。

【0034】実施例1～10 比較例1～15

図1に示される装置を用い、球状アルミナ粉末及び球状シリカ粉末を種々製造した。

【0035】球状アルミナ粉末は、粒子径1～200 $\mu$ mの水酸化アルミニウム粉末を、燃料ガス(LPG)と助燃ガス(酸素)とにより形成されている高温火炎中に、その供給量を種々変化させて供給し、熱分解・球状化処理を行った。火炎形成条件と原料供給量を変えて球状化率を調節すると共に、分級処理を行って種々の粒子径範囲をもつ球状アルミナ粉末の8種類(A1～A8)を製造した。その粒子径範囲と平均球形度を表2に示す。

【0036】球状シリカ粉末は、燃料ガス(LPG)10Nm<sup>3</sup>/hrと助燃ガス(酸素)25Nm<sup>3</sup>/hrとで30形成された高温火炎中に、天然珪石粉末(平均粒径5 $\mu$ m)を供給して球状化処理を行い、サイクロン及びバグフィルターから捕集された粉体を適宜分級・混合操作を行い、10種類の球状シリカ粉末(S1～S10)を製造した。その平均粒子径と平均球形度を表2に示す。

【0037】更に、市販品として、昭和電工社製球状アルミナ粉末「CBグレード」(記号イ)、アルコア化成社製非球状アルミナ粉末「CT4000SG-R」(記号ロ)について配合量を質量比で9:1となるように調製した。また、電気化学工業社製破碎窒化ケイ素粉末

40 「SN-F2」(記号ハ)、破碎結晶シリカ粉末(調製品)(記号ニ)、及び電気化学工業社製破碎シリカ粉末「FS-784」(記号ホ)を準備し、平均粒子径15 $\mu$ mに調整した。それらを表2に示す。

【0038】上記で準備された粉末を種々組み合わせて無機質粉末となし、それを表1に示される樹脂配合物に、表3及び表4に示される割合で充填し封止材を調製した。得られた封止材の(1)熱伝導率、(2)流動性及び(3)金型摩耗性を以下に従い測定した。それらの結果を表5に示す。

50 【0039】(1)熱伝導率は、封止材を直径28mm

m、厚さ3mmの円盤状に成型した後、熱伝導率測定装置（アグネ社製「ARC-TC-1型」）を用い、室温にて温度傾斜法にて測定した。

(2) 流動性は、スパイラルフロー金型を用い、EMM I-66 (EpoxyMolding Material Institute; Society of Plastic Industry) に準拠して行った。成型温度は175°C、成型圧力は7.4 MPa、成型時間\*

\*は90秒である。

(3) 金型摩耗性は、厚み6mm、孔径3mmのアルミニウム製ディスクの孔に175°Cに加熱された封止材を150cm<sup>3</sup>通過させた後のディスクの質量減少量を摩耗量として測定した。

【0040】

【表1】

材料の種類		配合割合 (%)
エポキシ樹脂	オツトクレゾールノボラック型 (日本化粧社製「EOCN-1020J」)	63.8
硬化剤	フェノールノボラック樹脂 (群榮化学社製「PSM-4261」)	32.1
硬化促進剤	トリフェニルホスフィン (北興化学社製)	0.6
離型剤	モタン酸エステル (クラリアンドジャパン社製 「WaxEflakes」)	3.5
シランカップリング剤	オルガノシラン (信越化学社製 「KBM403」)	フィラー量に対し外割 0.4

【0041】

※※【表2】

	アルミナ粉末		シリカ粉末	
	粒子径範囲(μm)	平均球形度	平均粒子径(μm)	平均球形度
A1	1~96	0.94		
A2	1~96	0.91		
A3	1~96	0.86		
A4	1~96	0.83		
A5	1~120	0.95		
A6	1~120	0.82		
A7	3~96	0.85		
A8	3~192	0.85		
S1			0.8	0.98
S2			0.5	0.97
S3			0.3	0.97
S4			0.2	0.91
S5			0.4	0.91
S6			0.8	0.90
S7			0.8	0.87
S8			1.2	0.92
S9			0.2	0.88
S10			0.4	0.88
他社製アルミナ粉(イ、ロ)及び各種既存粉末				
イ	粒子径範囲10~50μm	球形度0.84		
ロ	平均粒子径0.6μm	非球状化品		
ハ	平均粒子径15μm	非球状化品		
ニ	平均粒子径15μm	非球状化品		
ホ	平均粒子径15μm	非球状化品		

【0042】

【表3】

	無機質粉末の構成比率 (%)										樹脂への充填量 (vol.%)	
	アルミナ粉末				シリカ粉末							
	A 1	A 2	A 3	S 1	S 2	S 3	S 4	S 5	S 6			
実施例 1	97			3							70	
実施例 2	97			3							75	
実施例 3	80				20						70	
実施例 4	80				20						75	
実施例 5		70				30					70	
実施例 6		70				30					75	
実施例 7	90						10				75	
実施例 8	90							10			75	
実施例 9	90								10		75	
実施例 10			90							10	75	

【0043】

\* \* 【表4】

	無機質粉末の構成比率 (%)													樹脂への充填量 (vol.%)		
	アルミナ粉末						シリカ粉末						その他			
	A 1	A 4	A 5	A 6	A 7	A 8	S 1	S 7	S 8	S 9	S 10	イ	ロ	ハ	ニ	ホ
比較例 1	65						35									
比較例 2	100															
比較例 3		90					10									
比較例 4		90					10									
比較例 5			90				10									
比較例 6				90			10									
比較例 7					90	10										
比較例 8	90						10									
比較例 9	90							10								
比較例 10	90								10							
比較例 11	90									10						
比較例 12											90	10				
比較例 13												100				
比較例 14												100				
比較例 15																100

\* 樹脂への充填量は全て内割で 70 vol. %

【0044】

【表5】

	熱伝導率 (W/m·K)	流动性 (cm)	金型摩耗量 (mg)
実施例1	3.5	118	3.0
実施例2	3.8	105	3.1
実施例3	3.3	130	2.4
実施例4	3.6	112	2.5
実施例5	3.0	145	1.9
実施例6	3.2	117	1.9
実施例7	3.4	100	2.1
実施例8	3.3	105	1.8
実施例9	3.4	102	1.9
実施例10	3.5	100	2.8
比較例1	2.1	91	5.3
比較例2	3.5	67	5.8
比較例3	3.2	73	5.3
比較例4	3.5	79	6.5
比較例5	3.3	65	7.2
比較例6	3.2	76	5.2
比較例7	3.1	62	6.4
比較例8	3.0	73	5.1
比較例9	2.9	56	5.6
比較例10	3.1	81	4.7
比較例11	3.1	82	4.5
比較例12	3.0	26	6.6
比較例13	3.9	20	21.0
比較例14	2.4	45	16.0
比較例15	1.2	40	12.5

\* 型摩耗性であることがわかる。すなわち、無機質粉末が 70~75 vol. %と極めて高充填され、高熱伝導性を示しているにも拘わらず高流动性を示し、しかも金型摩耗量は、結晶シリカ粉末・破碎シリカ粉末・窒化ケイ素粉末を用いた場合に比べて、4分の1から10分の1程度であり、市販球状アルミナ粉末と比較しても半分以下である。

#### 【0046】

【発明の効果】本発明によれば、高熱伝導性・高流动性・低金型摩耗性を有する封止材等の樹脂組成物と、その製造に好適な無機質粉末が提供される。

#### 【図面の簡単な説明】

【図1】球状アルミナ粉末又は球状シリカ粉末の製造工  
程概略図

#### 【符号の説明】

1 溶融炉

2 バーナー

3 燃料ガス供給管

4 助燃ガス供給管

5 原料粉末供給管

6 重力沈降室

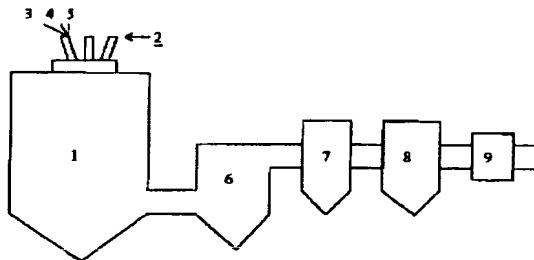
7 サイクロン

8 バグフィルター

9 ブロワー

【0045】表から明らかなように、本発明の無機質粉末の充填された封止材は、高熱伝導性・高流动性・低金型摩耗性である。

【図1】



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(54) HIGHLY THERMALLY CONDUCTIVE INORGANIC POWDER, RESIN COMPOSITION AND SURFACE TREATMENT AGENT COMPOSITION

(57)Abstract:

PROBLEM TO BE SOLVED: To provide highly thermally conductive inorganic powder which is used for preparing a resin composition having excellent heat radiation whose viscosity is not easily increased even when highly filled with the powder, and to provide the resin composition obtained by filling the powder into resin, and to provide a surface treatment agent composition used for producing the highly thermally conductive inorganic powder.

SOLUTION: The highly thermally conductive inorganic powder consists of inorganic powder having the average grain diameter of 1 to 20  $\mu\text{m}$ , and the maximum grain diameter of  $\leq 45 \mu\text{m}$ . The inorganic powder X being constituting grains of a grain size region of 3 to 40  $\mu\text{m}$  is the spherical one having roundness of  $\geq 0.80$ , and also has a thermal conductivity of  $\geq 10 \text{ W/mK}$ , and the inorganic powder Y being constituting grains of a grain size region is the spherical or aspherical one having roundness of  $\geq 0.30$  to  $< 0.80$ , and also has a thermal conductivity equal to or below that of the inorganic powder X, and in which the mass ratio of X/Y is 1 to 30. The highly thermally conductive inorganic powder may be treated by a surface treatment agent. The resin composition is filled with the highly thermally conductive inorganic powder. The surface treatment agent composition consists of specified two kinds of surface treatment agents.

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最終頁に統ぐ

(54)【発明の名称】 高熱伝導性無機粉末および樹脂組成物と表面処理剤組成物

(57)【要約】

【課題】樹脂に高充填しても容易に高粘度化せず、しかも放熱性に優れた樹脂組成物を調製することのできる、高熱伝導性無機粉末と、それを樹脂に充填した樹脂組成物と、高熱伝導性無機粉末を製造するのに用いられる表面処理剤組成物を提供する。

【解決手段】平均粒子径が1~20  $\mu\text{m}$ 、最大粒径が45  $\mu\text{m}$ 以下の無機粉末からなり、粒度域3~40  $\mu\text{m}$ の構成粒子である無機粉末Xの真円度が0.80以上の球状でしかも熱伝導率10 W/mK以上であり、粒度域0.1~1.5  $\mu\text{m}$ の構成粒子である無機粉末Yの真円度が0.30以上0.80未満の球状又は非球状でしかも熱伝導率が無機粉末Xと同等以下であり、X/Yの質量比が1~30であることを特徴とする高熱伝導性無機粉末。表面処理剤で処理された上記高熱伝導性無機粉末。これらの高熱伝導性無機粉末が充填された樹脂組成物。特定二種の表面処理剤からなる表面処理剤組成物。

## 【特許請求の範囲】

【請求項1】 平均粒子径が1～20μm、最大粒径が45μm以下の無機粉末からなり、粒度域3～40μmの構成粒子である無機粉末Xの真円度が0.80以上の球状でしかも熱伝導率10W/mK以上であり、粒度域0.1～1.5μmの構成粒子である無機粉末Yの真円度が0.30以上0.80未満の球状又は非球状でしかも熱伝導率が無機粉末Xと同等以下であり、X/Yの質量比が1～30であることを特徴とする高熱伝導性無機粉末。

【請求項2】 無機粉末Xが酸化アルミニウム粉末であり、無機粉末Yが酸化アルミニウム粉末及び/又はシリカ粉末であることを特徴とする請求項1記載の高熱伝導性無機粉末。

【請求項3】 シランカップリング剤、チタネート系カップリング剤及びアルミニート系カップリング剤から選ばれた1種又は2種以上の表面処理剤Aにて表面処理が施されていることを特徴とする請求項1又は2記載の高熱伝導性無機粉末。

【請求項4】 ポリカルボン酸系界面活性剤及び/又はポリアクリル酸系界面活性剤の表面処理剤Bにて表面処理が施されてなることを特徴とする請求項1、2又は3記載の高熱伝導性無機粉末。

【請求項5】 請求項1、2、3又は4記載の高熱伝導性粉末が充填されてなることを特徴とする樹脂組成物。

【請求項6】 シランカップリング剤、チタネート系カップリング剤、アルミニート系カップリング剤から選ばれた1種又は2種以上の表面処理剤Aと、ポリカルボン酸系界面活性剤及び/又はポリアクリル酸系界面活性剤の表面処理剤Bを、B/Aの質量比が1～30の割合で含有してなることを特徴とする高熱伝導性無機質粉末の表面処理剤組成物。

## 【発明の詳細な説明】

## 【0001】

【発明に属する技術分野】 本発明は、高熱伝導性無機粉末および樹脂組成物と表面処理剤組成物に関する。詳しくは、層厚が限られたところに使用される接着剤や、アンダーフィル等の半導体封止材等を製造するのに好適な高熱伝導性無機粉末と、それを樹脂に充填した樹脂組成物と、高熱伝導性無機粉末を製造するのに用いられる表面処理剤組成物に関するものである。

## 【0002】

【従来の技術】 電子機器の小型化、高機能化に伴い、電子部品の各所で用いられる樹脂組成物に充填される絶縁性無機粉末の微細化も進んでいる。例えば、半導体の実装方法の一つであるフリップチップ実装では、チップ保護に用いる封止材料（アンダーフィル材）を数10μm程度の基板とチップの隙間へ浸透させる為、液状エポキシ樹脂に微細な無機粉末を充填したアンダーフィル材が用いられている。

【0003】 しかしながら、無機粉末の充填量が多くなると、狭ギャップへ浸透しにくく、生産性が非常に悪くなるといった問題がある。これを解決するには樹脂組成物の粘度を下げる必要があり、低粘度ほど浸透性が向上する。こういった低粘度化はアンダーフィル材に限らず他用途の樹脂においても共通した課題であり、粘度に最も影響するのが充填される無機粉末の物性であると考えられている。特開2001-200139号公報には、アンダーフィル材用の無機充填材が開示され、2μm以下の粒子径をもつ粉末が無機粉末全体の50%以上がよいとされている。しかし、微粉が多くなると、樹脂組成物の粘度が容易に高粘度化するので、高充填化が困難となる。

【0004】 更に最近では、絶縁性の他に放熱性が求められる用途が出現し、充填材および樹脂の両面からの検討が進められている。従来、高熱伝導性無機粉末としては、窒化アルミニウム、酸化アルミニウム、結晶シリカ等が知られているが、その形状が破碎形状やカットエッジを有さない形状（丸味状）であるのでこれもまた樹脂組成物の粘度を容易に高め高充填させることができず、結果として満足する放熱性が得られない。また、これら粉末は樹脂との混合時に使用するニーダ、ロールや、成型時に用いる金型を激しく摩耗させてしまう為、生産性を悪化させてしまう。

## 【0005】

【発明が解決しようとする課題】 本発明は、上記に鑑みてなされたものであり、その目的は樹脂に高充填しても容易に高粘度化せず、しかも放熱性に優れた樹脂組成物を調製することができる、高熱伝導性無機粉末と、それを樹脂に充填した樹脂組成物と、高熱伝導性無機粉末を製造するのに用いられる表面処理剤組成物を提供することである。

## 【0006】

【課題を解決するための手段】 すなわち、本発明は以下のとおりである。

（請求項1） 平均粒子径が1～20μm、最大粒径が45μm以下の無機粉末からなり、粒度域3～40μmの構成粒子である無機粉末Xの真円度が0.80以上の球状でしかも熱伝導率10W/mK以上であり、粒度域0.1～1.5μmの構成粒子である無機粉末Yの真円度が0.30以上0.80未満の球状又は非球状でしかも熱伝導率が無機粉末Xと同等以下であり、X/Yの質量比が1～30であることを特徴とする高熱伝導性無機粉末。

（請求項2） 無機粉末Xが酸化アルミニウム粉末であり、無機粉末Yが酸化アルミニウム粉末及び/又はシリカ粉末であることを特徴とする請求項1記載の高熱伝導性無機粉末。

（請求項3） シランカップリング剤、チタネート系カップリング剤及びアルミニート系カップリング剤から選ばれた1種又は2種以上の表面処理剤Aと、ポリカルボン酸系界面活性剤及び/又はポリアクリル酸系界面活性剤の表面処理剤Bを、B/Aの質量比が1～30の割合で含有してなることを特徴とする高熱伝導性無機質粉末の表面処理剤組成物。

（請求項4） ポリカルボン酸系界面活性剤及び/又はポリアクリル酸系界面活性剤の表面処理剤Bにて表面処理が施されていることを特徴とする請求項1又は2記載の高熱伝導性無機粉末。

（請求項5） 請求項1、2、3又は4記載の高熱伝導性粉末が充填されてなることを特徴とする樹脂組成物。

れた1種又は2種以上の表面処理剤Aにて表面処理が施されていることを特徴とする請求項1又は2記載の高熱伝導性無機粉末。

(請求項4) ポリカルボン酸系界面活性剤及び/又はポリアクリル酸系界面活性剤の表面処理剤Bにて表面処理が施されてなることを特徴とする請求項1、2又は3記載の高熱伝導性無機粉末。

(請求項5) 請求項1、2、3又は4記載の高熱伝導性粉末が充填されてなることを特徴とする樹脂組成物。

(請求項6) シランカップリング剤、チタネート系カップリング剤、アルミネート系カップリング剤から選ばれた1種又は2種以上の表面処理剤Aと、ポリカルボン酸系界面活性剤及び/又はポリアクリル酸系界面活性剤の表面処理剤Bを、B/Aの質量比が1～30の割合で含有してなることを特徴とする高熱伝導性無機質粉末の表面処理剤組成物。

#### 【0007】

【発明の実施の形態】以下、更に詳しく本発明について説明する。

【0008】本発明の高熱伝導性無機粉末は、平均粒子径が1～20μmであり、かつ最大粒径が45μm以下であることが第1条件である。平均粒径が1μm未満であると、熱伝導率が著しく低下してしまい、20μmよりも大きいと混合機や金型等を激しく摩耗させてしまうので生産性が低下する。また、最大粒径が45μmよりも大きいと、樹脂組成物の粘度が容易に高まるだけでなく、粗大粒子が狭ギャップに詰まってしまい、樹脂組成物の浸透を妨げてしまい用途に制約を受ける。ここで、最大粒径とは、水篩法で篩上に残る残量が0.5質量%未満の粒径を意味する。

【0009】本発明の高熱伝導性無機粉末は、粒度域によって真円度の異なる2種以上の粉末が混合されたと同じような粒度構成を有している。もっとも、そのように混合されたものであってもよい。すなわち、本発明の高熱伝導性無機粉末は、無機粉末Xと無機粉末Yとを含み、粒度域3～40μmの構成粒子である無機粉末Xの真円度が0.80以上の球状でしかも熱伝導率10W/mK以上であり、粒度域0.1～1.5μmの構成粒子である無機粉末Yの真円度が0.30以上0.80未満の球状又は非球状でしかも熱伝導率が無機粉末Xと同等以下であることが第2条件となる。

【0010】本発明において、無機粉末Xを粒度域3～40μm、無機粉末Yを粒度域0.1～1.5μmに選定した理由は、多くの実験の結果、これらの粒度域の粉末を制御することによって樹脂組成物の粘度、熱伝導率ともに最も良好になることを見いだしたことによる。また、無機粉末Xの真円度が0.80未満であると、この無機粉末が樹脂組成物の粘性に最も大きな影響を与えていることから、樹脂組成物が容易に高粘度化されて高充填が困難となる。更に、その熱伝導率が10W/mK未

満であると十分に高い放熱特性を樹脂組成物に付与することができない。一方、無機粉末Yは樹脂組成物の熱伝導率に大きく影響しないが、無機粉末X同士間に入り込んで熱パスを助長する効果がある。従って、真円度が0.30未満であると無機粉末X同士間への進入が困難となり、0.8以上では無機粉末Xとの接触点が減ってしまい、熱パス助長効果も低下してしまう。また、その熱伝導率が無機粉末Xのそれを超えても、樹脂組成物の熱伝導率は無機粉末Xに大きく影響されているので、熱伝導率はそれほど向上せず、無機粉末Yとして、無機粉末Xよりも熱伝導率の大きなものを用いてもよいが、わざわざ比較的高価な熱伝導率の大きな粉体を用いることの意義が小さい。

【0011】ここで、真円度は、走査型電子顕微鏡（日本電子社製「JXA-8600M型」）と画像解析装置（日本アビオニクス社製）を用いて測定することができる。すなわち、粉末のSEM写真から粒子の投影面積

(A)と周囲長(PM)を測定する。周囲長(PM)に対応する真円の面積を(B)とすると、その粒子の真円度はA/Bとして表される。そこで、試料粒子の周囲長(PM)と同一の周囲長を持つ真円を想定すると、 $PM = 2\pi r$ 、 $B = \pi r^2$ であるから、 $B = \pi \times (PM/2\pi)^2$ となり、この粒子の真円度は、真円度 = A/B =  $A \times 4\pi / (PM)^2$ として算出することができる。そこで、本発明においては、任意100個の粒子について測定し、その平均値もって粉末の真円度とする。

【0012】無機粉末Xの具体例は、酸化アルミニウム、酸化亜鉛、窒化アルミニウム、窒化珪素、窒化硼素などの粉末であるが、化学的安定性、熱伝導性の点から

酸化アルミニウム粉末が最適である。一方、無機粉末Yの具体例は、結晶シリカ、溶融(非晶質)シリカ、炭酸カルシウム、酸化アルミニウム、水酸化アルミニウム、窒化アルミニウム、窒化硼素、窒化珪素等の粉末であるが、無機粉末Xが酸化アルミニウム粉末である場合、結晶シリカ粉末、溶融(非晶質)シリカ粉末、酸化アルミニウム粉末のいずれか一方又は組み合わせであることが最適である。

【0013】本発明の高熱伝導性無機粉末は、無機粉末Xと無機粉末Yの割合が、X/Yの質量比で1～30であることが第3条件である。無機粉末Yは、無機粉末Xによる樹脂組成物の低粘度を助長し、樹脂への高充填を可能にする。X/Y比が1未満であると微粉域の割合が少なすぎて樹脂組成物が容易に高粘度化し、また30超となると熱伝導性付与効果が著しく低下する。本発明の高熱伝導性無機粉末は、無機粉末Xと無機粉末Yの合計が60%以上(100%を含む)で構成されていることが好ましく、その合計が100%未満である場合の残部は、真円度0.80以上でしかも1.5～3μmの球状無機粉末で構成されていることが好ましい。

【0014】次に、他の本発明について説明する。これ

らの発明は、樹脂組成物の熱伝導性を更に向上させることができる高熱伝導性無機粉末であり、上記本発明の高熱伝導性無機粉末（以下、「高熱伝導性無機粉末基材」ともいう。）の改良に関するものである。

【0015】その1は、高熱伝導性無機粉末基材をシラン系カップリング剤、チタネート系カップリング剤及びアルミニート系カップリング剤から選ばれた一種又は二種以上の表面処理剤Aにて表面処理された高熱伝導性無機粉末（以下、「高熱伝導性無機粉末A」ともいう。）である。これを用いることによって、樹脂との密着性が更に高められ、高熱伝導性無機粉末Aと樹脂間での界面熱抵抗が低下し、更なる高熱伝導性を付与することができる。表面処理剤Aとしては、高熱伝導性無機粉末基材との反応性の点からシラン系カップリング剤が好ましい。

【0016】シランカップリング剤としては、ビニルトリクロルシラン、ビニルトリエトキシシラン、ビニルトリメトキシシラン、 $\gamma$ -メタクリロキシプロピルトリメトキシシラン、 $\beta$ -(3,4エポキシシンクロヘキシル)エチルトリメトキシシラン、 $\gamma$ -グリシドキシプロピルトリメトキシシラン、 $\gamma$ -グリシリメトキシプロピルメチルジエトキシシラン、N- $\beta$ -(アミノエチル) $\gamma$ -アミノプロピルトリメトキシシラン、N- $\beta$ -(アミノエチル) $\gamma$ -アミノプロピルトリエトキシシラン、N-フェニル- $\gamma$ -アミノプロピルトリメトキシシラン、 $\gamma$ -メルカプトプロピルトリメトキシシラン、 $\gamma$ -クロロプロピルトリメトキシシラン等であり、これらを一種または二種以上が用いられる。

【0017】表面処理剤Aによる高熱伝導性無機粉末基材の表面処理方法は、流体ノズルを用いた噴霧方式、せん断力のある攪拌、ボールミル、ミキサー等の乾式法、水系または有機溶剤系等の湿式法を採用することができる。せん断力は、高熱伝導性無機粉末基材の破壊が起こらない程度にして行うことに注意が必要である。

【0018】乾式法における系内温度ないしは湿式法における処理後の乾燥温度は、表面処理剤Aの種類に応じ熱分解しない領域で適宜決定される。例えば、 $\gamma$ -アミノプロピルトリエトキシシランである場合の温度は、80~150℃が望ましい。

【0019】その2は、アンダーフィル材のように樹脂組成物が低粘度である場合、高熱伝導性無機粉末が沈降して樹脂組成物の熱伝導性が損なわれないようにするため、ポリカルボン酸系界面活性剤、ポリアクリル酸系界面活性剤界面活性剤から選ばれた一種または二種以上の表面処理剤Bによって、高熱伝導性無機粉末基材又は高熱伝導性無機粉末Aを表面処理した高熱伝導性無機粉末（以下、両者を総称して「高熱伝導性無機粉末B」ともいう。また、前者による処理粉を「高熱伝導性無機粉末b1」、後者による処理粉を「高熱伝導性無機粉末b2」）である。

2」ともいう。）である。

【0020】表面処理剤Bによる、高熱伝導性無機粉末基材ないしは高熱伝導性無機粉末Aの表面処理は、表面処理剤Aの処理方法に準じて行われるが、表面処理剤Aの場合と同様に、表面処理剤Bの熱分解が起こらない温度で処理しなければならないことに注意が要る。

【0021】本発明においては、表面処理剤Aと表面処理剤Bとによる処理は、どちらか一方でもよく両方であってもよい。両方の処理によって、樹脂との密着性向上と高熱伝導性無機粉末の沈降防止を同時に低減することができ、樹脂組成物の放熱性を向上させることができる。

【0022】また、表面処理剤Aと表面処理剤Bによる両方の処理の場合、その処理は別々に行っても良く、また同時にに行っても効果がある。従って、表面処理剤Aと表面処理剤Bはあらかじめ混合された表面処理剤組成物であることが取り扱いの点で望ましく、その混合割合は、表面処理剤B/表面処理剤Aの質量比で1~30であることが好ましい。該比が、1未満であると、過剰な表面処理剤Aによって樹脂組成物の粘度上昇、表面処理剤Bの不足による十分な沈降防止効果が得られない。一方、該比が30超となると、過剰な表面処理剤Bによって、高熱伝導性無機粉末の表面処理剤A表面の吸着サイトが埋められ、表面処理剤Aの未反応が増加し、樹脂との密着性が十分に向上しない。

【0023】本発明の樹脂組成物は、上記した本発明の高熱伝導性無機粉末、すなわち高熱伝導性無機粉末基材、高熱伝導性無機粉末A、高熱伝導性無機粉末B（すなわち高熱伝導性無機粉末b1、高伝導性無機粉末b2）のいずれか単独または二種以上が充填されてなるものである。充填量は、用途によって異なり、50~95質量%が一般的である。

【0024】樹脂としては、エポキシ樹脂、シリコーン樹脂、フェノール樹脂、メラミン樹脂、ユリア樹脂、不飽和ポリエステル、フッ素樹脂、ポリイミド、ポリアミドイミド、ポリエーテルイミド等のポリアミド、ポリブチレンテレフタレート、ポリエチレンテレフタレート等のポリエステル、ポリフェニレンエーテル、ポリフェニレンスルフィド、全芳香族ポリエステル、ポリスルホン、液晶ポリマー、ポリエーテルスルホン、ポリカーボネート、マレイミド変性樹脂、ABS樹脂、AAS（アクリロニトリル-アクリルゴム・スチレン）樹脂、AES（アクリロニトリル・エチレン・プロピレン・ジエンゴム-スチレン）樹脂等が使用される。

【0025】樹脂組成物がアンダーフィル材のように液状樹脂組成物である場合、樹脂には液状エポキシ樹脂が用いられる。液状エポキシ樹脂としては、一分子中にエポキシ基を二個以上有するエポキシ樹脂であればいかなるものでも使用可能である。その具体例をあげれば、フェノールノボラック型エポキシ樹脂、オルソクレゾール

ノボラック型エポキシ樹脂、フェノール類とアルデヒド類のノボラック樹脂をエポキシ化したもの、ビスフェノールA、ビスフェノールF及びビスフェノールSなどのグリシジルエーテル、フタル酸やダイマー酸などの多塩基酸とエポクロルヒドリンとの反応により得られるグリシジルエステル酸エポキシ樹脂、線状脂肪族エポキシ樹脂、脂環式エポキシ樹脂、複素環式エポキシ樹脂、アルキル変性多官能エポキシ樹脂、 $\beta$ -ナフトールノボラック型エオキシ樹脂、1, 6-ジヒドロキシナフタレン型エポキシ樹脂、2, 7-ジヒドロキシナフタレン型エポキシ樹脂、ビスヒドロキシビフェニル型エポキシ樹脂、更には難燃性を付与するために臭素などのハロゲンを導入したエポキシ樹脂等である。この中でも常温で液状のエポキシ樹脂が好適に用いられるが、特にビスフェノールA型エポキシ樹脂、ビスフェノールF型エポキシ樹脂等のビスフェノール型エポキシ樹脂、脂環式エポキシ樹脂などが挙げられ、これらを一種または2種類以上が使用される。

【0026】液状エポキシ樹脂の硬化剤については、液状エポキシ樹脂と反応して硬化させるものであれば特に限定されず、例えば、フェノール、クレゾール、キシノール、レゾルシノール、クロロフェノール、*t*-ブチルフェノール、ノニルフェノール、イソプロピルフェノール、オクチルフェノール等の群から選ばれた1種又は2種以上の混合物をホルムアルデヒド、パラホルムアルデヒド又はパラキシレンとともに酸化触媒下で反応させて得られるノボラック型樹脂、ポリパラヒドロキシチレン樹脂、ビスフェノールAやビスフェノールS等のビスフェノール化合物、ピロガロールやフロログルシノール等の3官能フェノール類、無水マレイン酸、無水フタル酸や無水ピロメリット酸等の酸無水物、メタフェニジアミン、ジアミノジフェニルメタン、ジアミノジフェニルスルホン等の芳香族アミン等を挙げることができる。

【0027】本発明の樹脂組成物には、次の成分を必要に応じて配合することができる。すなわち、低応力化剤として、シリコーンゴム、ポリサルファイドゴム、アクリル系ゴム、ブタジエン系ゴム、スチレン系ブロックコポリマーや飽和型エラストマー等のゴム状物質、各種熱可塑性樹脂、シリコーン樹脂等の樹脂状物質、更にはエポキシ樹脂、フェノール樹脂の一部又は全部をアミノシリコーン、エポキシシリコーン、アルコキシリコーンなどで変性した樹脂など、シランカップリング剤として、 $\gamma$ -グリシドキシプロピルトリメトキシシラン、 $\beta$ -（3, 4-エポキシシクロヘキシル）エチルトリメトキシシラン等のエポキシシラン、アミノプロピルトリエトキシシラン、ウレイドプロピルトリエトキシシラン、N-フェニルアミノプロピルトリメトキシシラン等のアミノシラン、フェニルトリメトキシシラン、メチルトリメトキシシラン、オクタデシルトリメトキシシラン等の

疎水性シラン化合物やメルカプトシランなど、表面処理剤として、Zrキレート、チタネートカップリング剤、アルミニウム系カップリング剤など、難燃助剤として、 $Sb_2O_3$ 、 $Sb_2O_4$ 、 $Sb_2O_5$ など、難燃剤として、ハロゲン化エポキシ樹脂やリン化合物など、着色剤として、カーボンブラック、酸化鉄、染料、顔料などである。

【0028】本発明の樹脂組成物には、エポキシ樹脂と硬化剤との反応を促進するために硬化促進剤を配合することができる。その硬化促進剤としては、1, 8-ジアザビシクロ（5, 4, 0）ウンデセン-7、トリフェニルホスフィン、ベンジルジメチルアミン、2-メチルイミダゾール等がある。

【0029】本発明の樹脂組成物は、上記各材料の所定量を攪拌、溶解、混合、分散させることにより製造することができる。これらの混合物の混合、攪拌、分散等の装置は特に限定されないが、攪拌、加熱装置を備えたライカイ機、3本ロール、ボールミル、プラネタリーミキサー等を用いることができる。またこれらの装置を適宜組み合わせて使用してもよい。

【0030】本発明の樹脂組成物をアンダーフィル材として用いるとき、半導体チップと基板との間隙にそれを浸透させて封止する際の温度は60～120℃とすることが好ましい。

### 【0031】

【実施例】以下、実施例、比較例をあげて更に具体的に本発明を説明する。

#### 【0032】実施例1～7 比較例1～6

表1に示す無機粉末1～13を準備し、これを表2に示すような配合で混合し、高熱伝導性無機粉末基材イ～ホ（実施例1～5）と、チ～ワ（比較例1～6）を調整した。それらの粉末特性を表4に示す。また、高熱伝導性無機粉末ヘ（実施例6）および高熱伝導性無機粉末ト（実施例7）は、高熱伝導性無機粉末基材イを以下に従って表面処理し、本発明の高熱伝導性無機粉末Aおよび高熱伝導性無機粉末b1としたものである。

【0033】ボール径20mm、ボール充填率50体積%の10リットル容器内に、高熱伝導性無機粉末基材イを1kg、表3に示す表面処理剤A又は表面処理剤Bを40投入し、常温、常圧の条件下にて1回/秒の速度で1時間運転し、120℃にて1時間乾燥させ、高熱伝導性無機粉末ヘおよびトを得た。

【0034】表5に示される割合で各材料を混合し、これに高熱伝導性無機粉末イ～ワを無機粉末換算で75質量%の割合で混合し、樹脂組成物を製造した。これの粘度、熱伝導率、摩耗量を以下に従って測定した。それらの結果を表6に示す。

#### 【0035】（1）粘度

E型粘度計型（東京計器社製「EHD粘度計」）を用い、温度40℃、10rpmの回転数による粘度測定を

行った。

【0036】(2) 热伝導率

直径28mm、厚さ3mmの円盤状サイズ穴を設けた金型に樹脂組成物を流し込み、脱気後150°C×20分で成型した。热伝導率测定装置（アグネ社製「ARC-TC-1型」）を用い、室温において温度傾斜法で測定した。

\*

\* 【0037】(3) 摩耗量

厚み6mm、孔径3mmのアルミニウム製ディスクの孔に樹脂組成物を300mm<sup>3</sup>通過させた後のディスクの質量減少量を摩耗量として評価した。

【0038】

【表1】

無機粉末番号	無機粉末の種類	平均粒径 ( $\mu\text{m}$ )	無機粉末の 真円度	無機粉末の熱伝導率 (W/mK)
無機粉末1	酸化アルミニウム	15	0.95	30
無機粉末2	酸化アルミニウム	15	0.85	30
無機粉末3	酸化アルミニウム	8	0.90	30
無機粉末4	酸化アルミニウム	0.3	0.50	30
無機粉末5	酸化アルミニウム	0.5	0.75	30
無機粉末6	結晶シリカ	0.5	0.50	10
無機粉末7	非晶質シリカ	1	0.75	1
無機粉末8	酸化アルミニウムおよび 結晶シリカ(質量比1:1)	0.75	0.63	20
無機粉末9	非晶質シリカ	15	0.90	1
無機粉末10	酸化アルミニウム	15	0.70	30
無機粉末11	酸化アルミニウム	30	0.90	30
無機粉末12	酸化アルミニウム	0.5	0.95	30
無機粉末13	酸化アルミニウム	40	0.90	30

【0039】

30 【表2】

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	高熱伝導性 無機粉末記号	無機粉末Xの 種類	無機粉末Yの 種類	表面処理剤	無機粉末Xの 混合割合(質量%)	無機粉末Yの 混合割合(質量%)
実施例1	イ	無機粉末1	無機粉末4	なし	90	10
実施例2	ロ	無機粉末2	無機粉末5	なし	70	30
実施例3	ハ	無機粉末1	無機粉末6	なし	88	12
実施例4	ニ	無機粉末1	無機粉末7	なし	95	5
実施例5	ホ	無機粉末1	無機粉末8	なし	90	10
実施例6	ヘ	無機粉末1	無機粉末4	表面処理剤A	90	10
実施例7	ト	無機粉末1	無機粉末4	表面処理剤B	90	10
比較例1	チ	無機粉末9	無機粉末4	なし	90	10
比較例2	リ	無機粉末10	無機粉末4	なし	90	10
比較例3	ヌ	無機粉末1	無機粉末4	なし	20	80
比較例4	ル	無機粉末11	無機粉末4	なし	90	10
比較例5	ヲ	無機粉末2	無機粉末12	なし	70	30
比較例6	ワ	無機粉末13	無機粉末4	なし	50	50

【0040】

\* \* 【表3】

表面処理剤	種類	商品名	高熱伝導性無機粉末基材イ に対する添加率
表面処理剤A	シランカップリング剤	信越化学工業(株) 製 KBM-403	0.36質量%
表面処理剤B	ポリカルボン酸系界面活性剤	日本油脂(株) 製 マリアニムAKM-0531	2.0質量%

【0041】

【表4】

	高熱伝導性 無機粉末記号	平均粒径 ( $\mu$ m)	最大粒子径 ( $\mu$ m)	粒度域3~40 ル四側成粒子	粒度域0.1~1.5 ル四側成粒子	無機粉末X の真円度	無機粉末Y の真円度	質量比 X/Y
実施例1	1	12	45	酸化アルミニウム	酸化アルミニウム	0.95	0.50	9.0
実施例2	口	5	45	酸化アルミニウム	酸化アルミニウム	0.85	0.75	2.3
実施例3	ハ	11	45	酸化アルミニウム	結晶シリカ	0.95	0.50	7.3
実施例4	ニ	14	45	酸化アルミニウム	非晶質シリカ	0.95	0.75	19.0
実施例5	本	13	45	酸化アルミニウム	酸化アルミニウム	0.95	0.63	9.0
実施例6	ヘ	12	45	酸化アルミニウム	結晶シリカ			
実施例7	ト	12	45	酸化アルミニウム	酸化アルミニウム	0.95	0.50	9.0
比較例1	チ	12	45	非晶質シリカ	酸化アルミニウム	0.95	0.50	9.0
比較例2	リ	12	45	酸化アルミニウム	酸化アルミニウム	0.70	0.50	9.0
比較例3	ヌ	0.8	45	酸化アルミニウム	酸化アルミニウム	0.95	0.50	0.3
比較例4	ル	28	45	酸化アルミニウム	酸化アルミニウム	0.90	0.50	9.0
比較例5	ヲ	5	45	酸化アルミニウム	酸化アルミニウム	0.85	0.90	2.3
比較例6	ワ	18	75	酸化アルミニウム	酸化アルミニウム	0.90	0.50	1.0

【0042】

\* \* 【表5】

材料の種類	材料の種類	配合割合 (質量%)
エポキシ樹脂	ビスフェノールF型 液状エポキシ樹脂	
硬化剤	ジアミンジフェニルメタン	77.3
触媒	トリアミノメチルフェノール	22.2
		0.5

【0043】

【表6】

	高熱伝導性無機粉末 記号	粘度 (Pa·s)	熱伝導率 (W/mK)	摩耗量 (10 <sup>-3</sup> g)
実施例1	イ	30.5	2.3	2.1
実施例2	ロ	35.5	2.2	2.3
実施例3	ハ	36.5	2.2	2.0
実施例4	ニ	28.5	2.1	2.0
実施例5	ホ	32.5	2.3	2.2
実施例6	ヘ	31.1	2.6	2.2
実施例7	ト	32.6	2.6	2.1
比較例1	チ	36.2	0.4	1.8
比較例2	リ	68.5	2.4	10.5
比較例3	ヌ	85.5	1.2	1.2
比較例4	ル	76.3	2.3	9.5
比較例5	ヲ	38.5	0.9	2.1
比較例6	ワ	78.9	2.3	5.1

【0044】表1～6から明らかなように、本発明の高熱伝導性無機粉末を用いた樹脂組成物は、粘度、熱伝導性、摩耗性の全てにおいて、比較例よりも優れていることが分かる。

#### 【0045】実施例8、9

表面処理剤Aおよび表面処理剤Bからなる表面処理剤組成物を用いて試験を行った。すなわち、高熱伝導性無機粉末基材イ、表面処理剤A：シランカップリング剤（商品名：信越化学工業製KBM-403）、表面処理剤B：ポリカルボン酸系界面活性剤（商品名：日本油脂株式会社製マリアニムAKM-0531）を用いて試験を\*

\*行った。

【0046】表面処理方法は、ボール径20mm、ボール充填率50体積%の10リットル容器内に高熱伝導性無機粉末基材イを1kg、表面処理剤組成物を表面処理Aの質量換算で0.36gになるよう投入し、常温、常圧の条件下にて1回/秒の速度で1時間運転した後、120℃にて1時間乾燥させ、高熱伝導性無機粉末b2とした。その結果を表7に示す。

#### 30 【0047】

##### 【表7】

	表面処理剤組成物の 表面処理剤A/B質量比	粘度 (Pa·s)	熱伝導率 (W/mK)	摩耗量 (10 <sup>-3</sup> g)
実施例8	2	30.2	3.0	2.1
実施例9	20	30.8	2.9	1.9

【0048】表7からも明らかなように、表面処理剤Aと表面処理剤Bの混合物からなる表面処理剤組成物であっても十分に高く樹脂組成物の熱伝導率が向上することが分かる。

#### 【0049】

【発明の効果】本発明によれば、樹脂に高充填しても容

易に高粘度化せず、しかも放熱性に優れた樹脂組成物を40 調製することのできる、高熱伝導性無機粉末と、それを樹脂に充填した樹脂組成物と、高熱伝導性無機粉末を製造するのに用いられる表面処理剤組成物とが提供される。

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